New Jersey Water Resources Research Institute
Annual Technical Report
FY 2013

Introduction

The New Jersey Water Resources Research Institute (NJWRRI) supports a diverse program of research projects and information transfer activities. With oversight from the Advisory Council, which sets the Institute's Research Priorities, the available funds are divided between supporting faculty with 'seed' projects or new research initiatives and funding graduate students to develop their thesis research. The funding is intended to initiate novel and important research efforts by both faculty and students, thus emphasizing new research ideas that do not have other sources of funding. We hope to support the acquisition of data that will enable further grant submission efforts and in the case of students, lead to research careers focused on cutting-edge research topics in water sciences.

The goal of our information transfer program is to bring timely information about critical issues in water resource sciences to the public and to promote the importance of research in solving water resource problems. The program continues to develop the NJWRRI website (www.njwrri.rutgers.edu) into a comprehensive portal for water information for the state. We also collaborate with other state and regional organizations in sponsoring and producing conferences.

Research Program Introduction

The New Jersey Water Resources Research Institute has a policy, yearly reaffirmed by the NJWRRI Advisory Council, of using research dollars to promote novel directions of water resources research. To this end, ten grants−in−aid were awarded in FY2013 to graduate students who are beginning their research. We expect that the research is exploratory and is not supported by other grants. The intent is that these projects will lead to successful proposals to other agencies for further support. The larger goal of the research component of the Institute's program is to promote the development of scientists who are focused on water resource issues of importance to the state.

An NIWR/USGS National Competitive Grant Program project from New Jersey received continued funding in FY2013. Additional findings from that research are reported here. Also included are updates on two projects from FY2012.

Drought and Flood in the Eastern US

Basic Information

Title:	Drought and Flood in the Eastern US
Project Number:	2011NJ292G
Start Date:	9/1/2011
End Date:	8/31/2013
Funding Source:	104G
Congressional District:	12th
Research Category:	Climate and Hydrologic Processes
Focus Category:	Drought, Floods, Water Supply
Descriptors:	
Principal Investigators:	James Smith, Justin Sheffield, Eric Wood

Publications

1. Kam, J., J. Sheffield, X. Yuan, and E.F. Wood. 2013. The Influence of Atlantic Tropical Cyclones on Drought over the Eastern US (1980-2007). J. Climate, 26 (10), 3067-3086. http://dx.doi.org/10.1175/JCLI-D-12-00244.1.
2. Wright, D.B., J.A. Smith, G. Villarini, and M.L. Baeck. 2012. The hydroclimatology of flash flooding in Atlanta. Water Resources Research, 48, W04524, doi:10.1029/2011WR011371.
3. Kam, J., J. Sheffield, X. Yuan, and E.F. Wood. 2012. The Influence of Atlantic Tropical Cyclones on Drought over the Eastern US (1980-2007), Abstract H51D-1369, 2012 Fall Meeting, AGU San Francisco, CA. 3-7 Dec. (poster presentation)
4. Bates, N. S., J. A. Smith and G. Villarini, Flood frequency in forested central Appalachian watersheds, Water Resources Research, in review, 2014.
5. Cunha, L. K., P. Lin, J. A. Smith and M. L. Baeck, Hydrologic modeling of extreme floods in the Delaware River Basin, in preparation, 2014.
6. Kam, J., J. Sheffield, and E. F. Wood, 2014a: A multi-scale analysis of drought and pluvial mechanisms for the Southeastern United States. J. Geophys. Res., in revision.
7. Kam, J., J. Sheffield, and E. F. Wood, 2014b: Changes in Drought Risk over the contiguous United States (1901-2012): The influence of the Pacific and Atlantic Oceans. Geophys. Res. Letts., in revision.
8. Kam, J., J. Sheffield, and S. Sadri, 2014c: Lowflows over the Eastern US and its Association with local antecedent rainfall and large-scale climate indices (1962-2011) HESSD, to be submitted.
9. Lu, P., L. K. Cunha, J. A. Smith, M. L. Baeck and N. Lin, On the distribution of flood peak magnitudes over a drainage network, in preparation, 2014.
10. Liu, M., J. A. Smith and G. Vecchi, Extreme rainfall from landfalling tropical cycloes: Hurricane Irene case study, in preparation, 2014.
11. Sadri, S., J. Kam, and J. Sheffield, 2014: Nonstationarity of low flows and their timing in the Eastern United States. Water Resour. Res., in revision.
12. Sadri, S., J. K. Roundy, and J. Sheffield, 2014: Low flow estimation for the eastern United States using the VIC hydrological model. HESSD. to be submitted.
13. Smith, J. A., M. L. Baeck, and G. Villarini, Flood hydroclimatology of the East Branch Delaware River basin, in preparation for submission to J. of Hydrometeorology, 2014a.
14. Smith, J. A., G. Villarini and M. L. Baeck, Flood hydroclimatology of the Potomac River Basin, in preparation for submission to Water Resources Research, 2014b.

15. Wright, D. B., J. A. Smith, G. Villarini, and M. L. Baeck, Estimating the frequency of extreme rainfall using weather radar and stochastic storm transposition, J. of Hydrology, in press, 2014a.
16. Wright, D. B., J. A. Smith, G. Villarini, and M. L. Baeck, Long-term, high-resolution, radar rainfall records for urban hydrology, J. of the American Water Resources Associations, in press, 2014b.
17. Wright, D. B. , J. A. Smith, amd M. L. Baeck, Flood frequency analysis using radar rainfall fields and stochastic storm transposition, Water Resources Research, in press, 2014c.
18. Kam, J., J. Sheffield, E. F. Wood, 2013, An integrative analysis of drought in the southeastern United States, 93rd AMS Annual Meeting, Abstract #221097, January 6-11th, Austin, TX
19. Kam, J., J. Sheffield, and E. F. Wood, The influence of sea surface temperatures on seasonal drought over the Conterminous United States (1901-2012): A Bayesian Approach, J13.4, 2-6 Feb, 2014, Atlanta, GA.
20. Sadri, S., and J. Sheffield (2012), Low flow trends in the eastern United States, Abstract H34D-03, presented at 2012 Fall Meeting, AGU San Francisco, Calif., 3-7 Dec (oral).
21. Sadri, S., and J. Sheffield (2013), Comparison of low flows from the VIC hydrological model with observations for the eastern United States, Abstract H33G-1475, presented at 2013 Fall Meeting, AGU San Francisco, Calif., 3-7 Dec (poster).

(4) Project Summary:

Problem and Research Objectives -

We propose to develop statistical procedures for regional analyses of drought and flood in the eastern US based principally on USGS stream gaging data. We will focus on the interrelationships between drought and flood, with a particular emphasis on water supply systems for large urban centers of the eastern US. Procedures will exploit mixture distribution representations of flood and drought variables; these representations center on tropical cyclones, which are major rainfall and flood agents during summer and fall, and extratropical systems, which are major rainfall and flood agents during spring and fall in the eastern US. We adopt a regional approach covering the eastern US due to the scale of the weather and climate systems at play. Special emphasis will be placed in this study on the Delaware River basin (water supply for New York City), the Potomac River basin (water supply for Washington D. C.), the Catawba River basin (water supply for Charlotte, North Carolina) and the Chattahoochee River basin (water supply for Atlanta, Georgia). The procedures that we will develop are designed for broad use by USGS National and District offices for water resource assessment studies. Additional users will include river basin planning and management agencies (including the Delaware River Basin Commission and Interstate Commission on the Potomac River Basin), states and local municipalities.

The procedures will be used for regional assessments of drought and flood frequency, short-term (seasonal to interannual) characterization of drought and flood occurrence and long-term trend assessment of drought and flood variables. These procedures will provide capabilities for regional water resources analyses covering the eastern US. Detailed analysis capabilities will be developed for the Delaware, Potomac, Catawba and Chattahoochee River basins, providing information on drought and flood frequency for major urban centers of the eastern US.

The broad objective of this study is to develop statistical tools for characterization of water resources and flood hazards based on USGS streamflow records. The specific objectives of the study are to develop statistical procedures for: 1) assessing non-stationarities of drought and flood variables (in terms of change-points, slowly varying trends and long-term persistence), 2) characterizing spatial extremes of drought and flood and 3) characterizing the interrelationships between drought and flood, including their relationships to climate indices. The project will be carried out over a two year time period. Development of data sets and statistical procedures was completed during year 1. Implementation of procedures for assessing non-stationarities in drought and flood variables was also completed in year 1. In the second year of the project, we will complete analyses of the interrelationship of drought and flood for the eastern US, analyses of spatial extremes and analyses of drought and flood occurrence in terms of climate indices. We will also synthesize analyses for the Delaware, Potomac, Catawba and Chattahoochee River basins during year 2.

Methodology -

We analyzed the spatio-temporal patterns of low flows across the eastern US to: 1) identify non-stationarity that may be due to anthropogenic or climatic influences; 2) to identify sites with long records (multiple decades) to analyze long-term trends and variability, including sub-series of data that are identified as stationary with respect to anthropogenic influences; (3) to quantify the variability of low flow volumes and timing, and their attribution. We used nonparametric tests to identify abrupt and gradual changes in time series of low flows and their timing for 508 USGS streamflow gauging sites in the eastern US with more than 50 years of daily data, to systematically distinguish the effects of human intervention from those of climate variability. Daily streamflow records were originally collected for 4878 sites from the USGS National Water Information System. 508 sites based were selected based on length of record (> 50 years), whether the site is currently active or stopped being active after year 2000, and no missing years of daily data. The selected stations have a record of at least 50 years worth of daily data. Figure 1 shows the location of the 508 sites colored by their drainage area [mi^2]. Table 1 shows the record length statistics of the 508 sites.

We analyzed four variants of low flows, based on different time scales. The 1-day Q_1 minimum low flow is the annual minimum daily streamflow. For each year, two values were calculated: the flow on that day in [ft^3/s] and the date ($\in[1,365]$) on which it occurred. The other three variants Q_7, Q_{30}, and Q_{90} are obtained by applying the same analysis to 7-day, 30-day, and 90-day moving average time series. A time series decomposition algorithm was applied to the n-day annual time series to identify non-stationary series and stationary sub-series that could be used for further analysis. We applied three tests to identify weak stationarity: (1) the Ljung-Box test, which tests for autocorrelation; (2) the Mann-Kendall test, which tests for monotonic increasing or decreasing trends; and (3) the Pettitt test, which tests for abrupt changes or change points. For each site, we also examined the date of occurrence, to test whether the timing of low flows was stationary or not. We used a measure of variability to determine, among all years, the size of the window of occurrence in which the flow occurs. For *n* low flow occurrence dates of $x_i, x_j, \ldots, x_n$, we defined the variability as the root mean square of the time differences of the x_i.

We also analyzed the contribution of tropical cyclones (TC) to the delayed initiation and early recovery of drought in the eastern US. Given that tropical cyclones can bring up to 30% of total seasonal rainfall in the southeast, we hypothesized that they also contribute significantly to drought recovery. As far as we know, this is the first study to evaluate the impact of Atlantic tropical cyclones on drought in a quantitative manner. The HURDAT (Jarvinen et al. 1984; Neumann et al. 1993) was used to identify TC-related rainfall (1980-2007) from the hourly rainfall dataset of NLDAS2 (Xia et al., 2012). The Atlantic HURDAT data include track information for cyclones from 1985-2011 including the center of TC at 6 hourly timestep, the maximum wind speed, minimum pressure, and the category. Recent studies (Landsea et al, 2010; Kunkel et al., 2010) have used the HURDAT data to analyze the historical trends in the duration of TCs and to examine the contribution of TCs to heavy rainfall. As the NLDAS-2 forcing data have an hourly temporal resolution, the HURDAT tracks locations are linearly interpolated from 6 hourly to hourly following (Villarini et al., 2011). TC-related rainfall is then estimated using a distance threshold value as in previous studies (Shepherd et al, 2007; Jiang and Zipser, 2009; Barlow, 2011). The chosen value of the threshold of 5-degrees (about 500km) was estimated from a sensitivity analysis. To understand the contribution of TCs to drought recovery (as well as late initiation), we ran the VIC land surface model with and without the contribution of tropical cyclone rainfall. Drought was defined in terms of soil moisture percentiles relative to a set of thresholds and durations to represent various types of drought from short-term severe to long-term moderate droughts.

Studies of flood climatology have focused on the Potomac River basin (Smith et al. 2014b and Bates et al. 2014), the Delaware River basin (Smith et al. 2014a), the Chattahoochee River basin (Wright et al. 2012) and Catawba River basin (Wright et al. 2013). The Potomac River stream gaging stations at Point of Rocks, Maryland has one of the longest records in the stream gaging archive of the USGS. Furthermore, the Potomac River basin is one of the least "regulated" river basins in the eastern US, with a single reservoir (controlling less than 3% of the drainage basin) having been completed in the early 1980s. We have examined change points and trends in annual flood peak data and peaks-over-threshold flood data for the Point of Rocks station. In addition to the Point of Rocks station, the Potomac River basin has a relatively large density of stream gaging stations with more than 50 years of record. We have carried out analyses of change points and trends for all of the "long" stream gaging records in the Potomac basin (Smith et al. 2014b). We have also examined the role of orographic thunderstorm systems as catastrophic flood agents in the central Appalachians (Bates et al. 2014).

The Delaware River basin is a critical water supply source for New York City and exhibits large spatial gradients in the runoff and flood magnitudes. There is a dense network of USGS stream gaging stations in the East Branch Delaware River basin linked to assessments of hydrology and water quality of the Pepacton reservoir. The Delaware River basin has experienced a sequence of major flood events, with Hurricane Irene causing extensive damage and loss of life in August 2011. We have developed high-resolution rainfall analyses for major flood events in the Delaware and examined spatial variability and heterogeneity in extreme rainfall, runoff and flood magnitudes (Liu et al. 2014, Cunha et al. 2014, Lu et al. 2014 and Smith et al 2014a).

Atlanta, Georgia and Charlotte, North Carolina have been rapidly urbanizing regions of the southeastern US. We have examined the hydroclimatology and hydrology of flooding in the Atlanta metropolitan region (within the Chattachoochee River basin ; Wright et al. 2012) and the Charlotte, Metropolitan region (within the Catawba River basin; Wright et al. 2014 a - c).

Principal Findings and Significance - please provide a progress report if the project is to be continued; if a final report, summarize significant findings. All graphics and tables should be included within the body of the document.

a) Analysis of Low Flows over the Eastern US

The recursive decomposition algorithm was used to systematically identify step changes in the low flow series and reapply the algorithm on the two sub-series to identify useable series. Figure 2 summarizes the time periods that were identified as useable at each step of the recursive algorithm for all sites for Q_1. The light blue lines represent the original record length for each site. The vertical axis shows the site number from 1 to 508 ordered from the lowest to highest latitude. Therefore, site 1 is the most southerly and site 508 is the most northerly. The left panel of Figure 2 shows the record length of sites which, in the first step of categorization, had no significant autocorrelation. These sites are colored according to their trend value (calculated using the Mann-Kendall test): 0 (no significant trend), -1 (significant negative trend), or 1 (significant positive trend). The middle panel of Figure 2 again shows the original record length for each site in light blue, but highlights the sites that were identified with an abrupt step change by the Pettitt test and were split into two parts. For each part that exhibits no autocorrelation, the trend values were calculated. The right panel shows the parts of the time series that were recovered in the next step of the decomposition algorithm. As long as the record length is greater than or equal to 30 years the algorithm is applied recursively on the remaining parts of the time series. The number of sites shown in the right panel is small but their data are still useful for subsequent analysis.

We compared these results with USGS site flags that provide qualitative information on anthropogenic influences (such as dams) and changes in the gauge measurements (such as a change in the gauge datum). Table 2 shows the breakdown of numbers of sites in each category of the decomposition algorithm (no trend, step change, etc) and the relation to USGS flags for Q_1 and Q_{90}, and indicates that in every category, anthropogenic changes are documented by the USGS. For Q_1, the majority of sites in categories 4 (64%; step change), and 5 (56%; significant autocorrelation) are flagged by the USGS as somehow affected. This suggests that the algorithm has some skill in identifying altered flow series. However, there are also many sites in category 1 (no trend; 45%), 2 (decreasing trend; 34%) and 3 (increasing trend; 67%) that are also flagged suggesting that anthropogenic impacts for these sites are minimal and/or are overwhelmed by any climate or land use induced changes. The fact that the majority of stationary sites (category 1) are not flagged is encouraging. From Table 2: If a site is flagged and its low flow series has a decreasing trend, this is mostly associated with a change of gauge datum; If a site is flagged and its low flow series has an increasing trend, this is mostly related to regulation or a change of gauge datum; If a site is flagged and it exhibits a step change, this is mostly associated with regulation, a change of gauge datum, or possibly urbanization; If a site is in category 5 (not considered further due to significant autocorrelation), it may be regulated or its gauge datum has changed; If a site shows no trend but is still flagged, it may be regulated or its gauge datum changed, but the statistics do not indicate a trend. This suggests that the impact of regulation was either minimal or good management practices have been put in place. The majority of these sites are located in the upper Mid-Atlantic in the states of New York, New Jersey, and Virginia.

We identified a time period (1959-2005) common to all sites for which they have useable data (no step changes), and calculated statistics of Q_n, including the trend, and the consistency of trends and correlation among Q_n values. Figure 3 shows the spatial pattern of the MK trend test values for Q_1 when autocorrelation is ignored (top left panel) and if we remove sites with significant autocorrelation (top right panel). The gray colored sites in the right panel are those with significant autocorrelation. In both of these panels, a pattern of increasing trend in low flows in the northeast and a decreasing trend in the southeast is apparent. However, ignoring the effect of autocorrelation may give rise to misleading results by showing a denser pattern of significant trends. The bottom left panel shows the results when sites that have USGS flags are also excluded, i.e. for sites without documented anthropogenic impacts. The attribution of trends at these sites is therefore likely related to climate variability/change and/or land use change, rather than a direct anthropogenic impact on the low flows. Overall, the consistency in trends among the Q_n series is generally uniformly distributed across the domain.

Figure 4 summarizes the distribution of the onset of the low flow season for Q_1, where the first season is defined as the 4-month period that contains the majority of low flow occurrences (top panels) and the second season as the 4-month period that contains the majority of the remaining low flows (bottom panels). The left panels show the onset month of the season and the right panel shows the probability of the onset season in that month. If the onset time of the low flow season for a site happens 70% to 100% in a specific month, that site is assumed to have only one low flow season. For sites with one low flow season, the onset of the season changes moving from north to south. Most of the sites north of North Carolina have low flow seasons starting in July, which is generally driven by the slight decline in precipitation during the autumn as well as the increased evaporation during the summer (Small et al., 2006). In Florida the season starts in April-May. For coastal sites, the season starts earlier (mostly in June), and for sites in the southwestern part of the domain, the season starts mostly in September-October. The sites that have low flow events occurring 40-69% of the time in one month and 20-40% of the time in a different month are characterized as having two low flows seasons. These sites are mostly in Florida, and along the coastline of Georgia, South and North Carolina, New York, New Jersey, and Maine and their second season occurs mostly in fall. For New York, New Jersey, some sites in the west coastline of Florida, the second low flow season mostly starts in November and December. Sites near the Gulf of Mexico and some sites in North Carolina have second low flow seasons starting in April. The second low flow season for the far northeast sites begins in December or January and can be related to freezing conditions that may store water as snow and river ice. We tested for trends in low flow timing but these were generally undetectable, although abrupt step changes at a few sites in the northeast appear to be associated with regulation (not shown).

b) Attribution of Abrupt Changes and Trends

The decomposition algorithm identified the subset of a time series that are likely hampered by management effects (non-stationary abrupt changes due to reservoir building and land use change), show long-term increases or decreases (non-stationary trends due to climate change or longer-term land use change) or are stationary. The latter set of sites is useful for low flow frequency analysis or generating flow duration curves, for example. Trends in low flows can be seen as potential evidence of climate change through changes in precipitation and temperature. Most of the sites (80%) in the eastern US do not show a significant trend. The other 20% of sites show increasing trends in low flows in the northeast and decreasing trends of low flows in the southeast. These results agree with those obtained from both observations and model simulations in terms of large scale changes in drought, low and mean flows (Small et al., 2006; Andreadis and Lettenmaier, 2006; Dai et al., 2004; Milly et al., 2005). Increases in low flows in the northeast are consistent with increasing precipitation, and may also be related to increasing temperatures that are impacting freezing soils and snow cover (Hayhoe et al., 2007) and therefore the late winter/early spring low flow period. The long-term trend results also are consistent with the pattern of land use change over the 20th century (USGS, 2012). The northeast and the southeast have had the most overall land use change over the last decades while the changes over the Appalachian Mountains have been more heterogeneous. Decreases in the southeast may be related to land cover change from timber harvesting and over extraction of groundwater. Further investigation of site-specific land use changes and timing is needed to provide more robust attribution of changes.

In most cases, larger dams have the most significant regulation impacts on the flows (Smakhtin, 2001), and these types of changes are generally identified in our analysis. Statistically, many sites show stationary behavior after identification of a regime shift by the Petitt test, suggesting that these sites are being effectively managed from the standpoint of the time series. A lower variability in the date of occurrence of low flows for a site also suggests either evidence of stationarity or a properly human managed system. The USGS site notes also provide corroborating evidence of the impact of management, such as the year of construction of a dam. However, the site notes do not always match up exactly with the results from the Pettitt test, which may be because the regulation does not take effect immediately or combined effects from, for example, land use change dampen or delay the changes. The analysis of low flow stationarity has been submitted as a journal paper (Sadri and Sheffield, 2014).

c) Drivers of Inter-Annual Variability in Low Flows

The attribution of the trends, variability and spatial characteristics of low flows was explored further in terms of teleconnections with large-scales climate features such as the Atlantic Multi-Decadal Oscillation and ENSO for a subset of 150 USGS sites with long time series (> 50 years). Inter-annual variability in low flows is generally controlled by antecedent precipitation but with different lead time and correlation strength depending on the geographical characteristics of the basin. In general, most of stations have a maximum temporal correlation coefficient between antecedent precipitation and 1-day low flows from 1 to 4-months lag (Figure 5). However, some stations in the mid-Atlantic and New England show much longer lags (8-month to 10-month), which may be a result of groundwater dominance or some form of undetected water management. Annual low flows are positively and significantly related to the summertime North Atlantic Oscillation (NAO) index over most of the southern part of the Northeastern U.S. (Figure 6). On the other hand, most stations are negatively correlated with the longer-term AMO during the preceding spring (MAM), suggesting a two season lag (not shown). This is similar to the findings of Enfield et al. (2001), except for smoothed mean stream flows. In the late-1990s, the AMO was switched from a negative phase to a positive phase and therefore may have played a role in the reduction of 1-day low flows in the southeast, with implications for water availability and environmental flows. These results will be submitted for journal publication as Kam et al (2014c) and have contributed to a broader study on drought mechanisms for the southeast (Kam et al., 2014a) and of drought risk over the whole U.S. (Kam et al., 2014b).

d) Impact of Tropical Cyclones on Drought

While TCs play an important role over the eastern US in terms of heavy rainfall events (Shepherd et al, 2007; Knight and Davis, 2009), our results indicate that their contributions to annual and TC-season total rainfall are quite small compared to non-TC related rainfall (Table 3). Regional average TC-related rainfall varies from 1% to 5% of the annual total. For each region, the standard deviation of TC-related rainfall exceeds the average value, whereas the annual total and non-TC related rainfall far exceeds their standard deviations, which in turn exceed that of the TC-related rainfall. As an example of a year with high TC activity, TCs in 2005 provided about 10% (>15%) of total annual (TC-season) total rainfall in the Midwestern region while its average regional contribution is 1% of annual total rainfall.

Using two VIC land surface model simulations (one with and one without TC rainfall) we quantified the impact of TCs on drought. Tropical cyclones variously impact soil moisture droughts via late drought initiation, weakened drought intensity, and early drought recovery. For the eastern US as a whole, Figure 7 summarizes the impact of tropical cyclones on drought in terms of the difference in the number of droughts between the simulations without and with TC rainfall, the number of days delay in drought initiation and the number of days earlier in drought recovery. TCs decreased the average duration of moderately severe short-term and long-term droughts by less than 4 (10% of average drought duration per year) and more than 5 (15%)days yr, respectively. Also, they removed at least two short-term and one long-term drought events over 50% of the study region. Despite the damage inflicted directly by TCs, they play a crucial role in the alleviation and removal of drought for some years and seasons, with important implications for water resources and agriculture. This work has been published in Journal of Climate as Kam et al. (2013).

e) Evaluation of the VIC hydrological model to simulate low flows

The ability of hydrological models to simulate low flows is important for understanding low flow generation mechanisms and changes, as well as the development of hydrological prediction systems for decision-making for water management. To understand this, we evaluated the VIC model for simulating low flows in the eastern U.S. We evaluated the current version of VIC, which is calibrated to monthly mean flows, for Q_7 low flows at the 508 USGS gauging sites for for 1959-2011. The 508 sites were filtered for significant autocorrelation to remove sites that showed signs of management or significant groundwater dominance that the model cannot simulate, leaving 432 sites. The results show that the current calibration of VIC is not sufficiently accurate for low flow-related applications. VIC generally underestimates low flow magnitudes (Figure 8), which is consistent with the lack of a specific groundwater component in the model, although the year-to-year variability is generally reproduced across most sites. Performance is better in the northeast compared to the southeast, which may be related to the lower correlation with antecedent precipitation and larger dominance of groundwater in the southeast. To understand whether the model results could be improved through re-calibration, we selected a sub-set of ten sites in the northeast and calibrated directly against Q_7 low flows for 1980-2004. The calibration improved the simulation of low flows considerably, with parameters that control baseflow showing the most sensitivity (Figure 9). Evaluation of simulated mean flows for the low flow calibration indicated similar performance to the mean flow calibration, suggesting that calibration to low flows (or multi-objective calibration to points on the flow duration curve) may be a better approach to simulating the broader flow regime. These results will be submitted as a journal article (Sadri and Sheffield, 2014).

f) Flood Studies

The Delaware River basin is an important water supply source for the New York City metropolitan region and contains a dense network of USGS stream gages (Figure 10). Hydroclimatological analyses of flooding in the Delaware have focused on nonstationarities in flood occurrence and spatial heterogeneities in precipitation, runoff and flood peaks (Smith et al 2014a). Orographic precipitation mechanisms play an important role in the flood hydroclimatology of the region (Figures 11 and 12; see Liu et al. 2014). Rainfall analyses have been carried out for sequence of major flood events in the Delaware River basin and used to assess precipitation controls of the striking contrasts in runoff and flood peaks in the Delaware River basin (Smith et al 2014a and Liu et al. 2014). Flooding from Hurricane Irene in August of 2011 produced devastating flooding and has been a focus of flood hydrology and flood hydrometeorology research (Figure 13; see Cunha et al. 2014, Lu et al. 2014 and Liu et al 2014).

Analyses have provided new tools for representing flood peak magnitudes over the entire drainage network through the “flood index”, i.e. the ratio of peak discharge to the 10-year flood magnitude (Figure 14; see Lu et al. 2014 and Cunha et al. 2014). A principal conclusion of these analyses is that orographic precipitation mechanisms play a dominant role in determining spatial heterogeneities of flood hazards.

Hydroclimatological analyses of flooding in the Potomac River basin have focused on “mixture” distributions, change points and trends and controls of upper tail behavior of flood peak distributions (Smith et al. 2014b). The dominant flood agents for the Potomac River at Point of Rocks are winter/spring extratropical systems, like the March 1936 flood that produced record flood peaks throughout major drainages of the eastern US. Tropical cyclones play an important role in determining upper tail properties and contribute to a fall peak in flood frequency. Orographic thunderstorm systems determine the upper tail of flood peak distributions in “small” (less than 100 km^2), forested central Appalachian watersheds (Bates et al 2014). Despite a history of major land use transformation, including deforestation in the late 19th and early 20th centuries, there is little evidence of nonstationarities in flood occurrences for the Potomac River at Point of Rocks.

Urban modification of land surface hydrology and precipitation hydroclimatology have profound impacts on flood hazards in major urban areas of the eastern US (Wright et al. 2012 and 2014 a - c). High-resolution radar rainfall fields provide useful tools for estimating flood frequency over urban drainage networks (Figure 15).

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Table 1: Record length statistics of the 508 USGS sites.

	Min	**Max**	**Average**	**Median**
Years	50	120	74	92

Category	Q_1	Q_{90}	Flag	Q_1	Q_{90}	Flag type	Q_1	Q_{90}
No Trend	221	334	Flagged	100	163	DamF	2	2
						RegPar	32	43
						Reg	32	61
						Urb	2	5
						ChangeDat	2	3
						ChangeDatH	30	49
			Not Flagged	121	171			
Decreasing Trend	36	30	Flagged	12	7	RegPar	0	1
						Low	1	1
						Reg	1	1
						ChangeDat	1	0
						ChangeDatH	9	4
			Not Flagged	24	23			
Increasing Trend	57	68	Flagged	38	48	RegPar	11	11
						Reg	17	28
						Urb	1	2
						ChangeDat	1	0
						ChangeDatH	8	7
			Not Flagged	19	20			
Step Change	155	54	Flagged	99	37	DamF	1	1
						RegPar	23	10
						Reg	61	18
						Urb	5	2
						ChangeDat	1	2
						ChangeDatH	8	4
			Not Flagged	56	17			
Out	39	22	Flagged	22	16	RegPar	4	5
						Reg	5	8
						Urb	1	0
						ChangeDat	1	1
						ChangeDatH	11	2
			Not Flagged	17	6			

Table 2: Comparison of the number of sites in each category of the decomposition algorithm and their USGS flags for Q1 and Q90. DamF: dam failure; RegPar: partially regulated; Reg: regulated; Low: flow below rating curve limit; Urb: affected by urbanization; ChangeDat: Change base discharge; ChangeDatH: change gauge datum.

Table 3: Mean and standard deviation of annual total rainfall, non-TC related rainfall, and TC-related rainfall and their standard deviations for 1980-2007.

Region	**Area (10^3 km^2)**	**Annual**		**Non-TC related**		**TC-related**	
		Mean [mm]	**Std [mm]**	**Mean [mm]**	**Std [mm]**	**Mean [mm]**	**Std [mm]**
MW	394	977	104	968 (99%)	105	9 (1%)	20
NE	387	1148	141	1122 (98%)	134	26 (2%)	34
S	389	1395	174	1355 (97%)	182	40 (3%)	53
SE	475	1319	152	1258 (95%)	157	61 (5%)	59

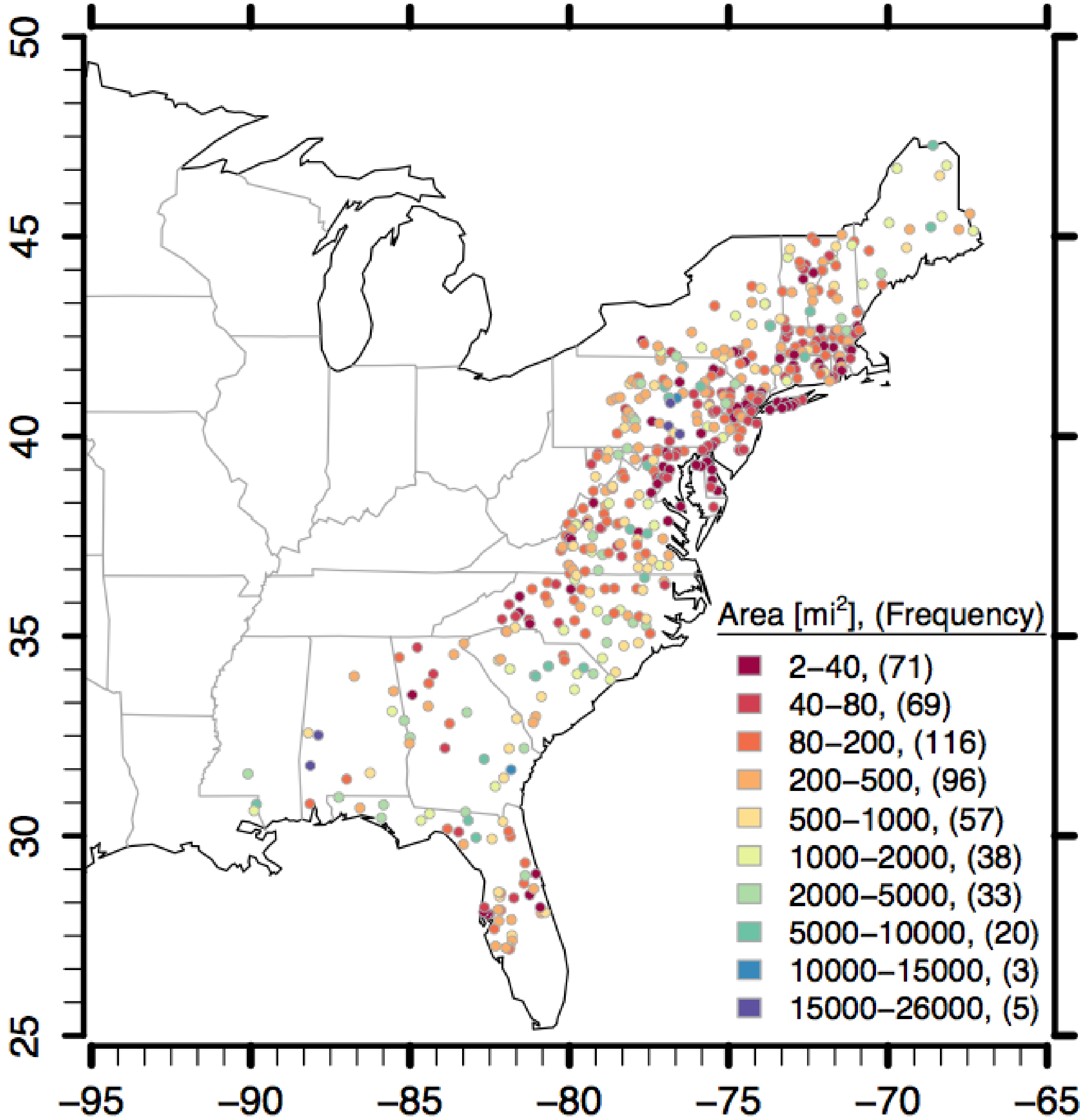


Figure 1: Location and basin areas of the 508 USGS sites with 50 years or more of complete daily data.

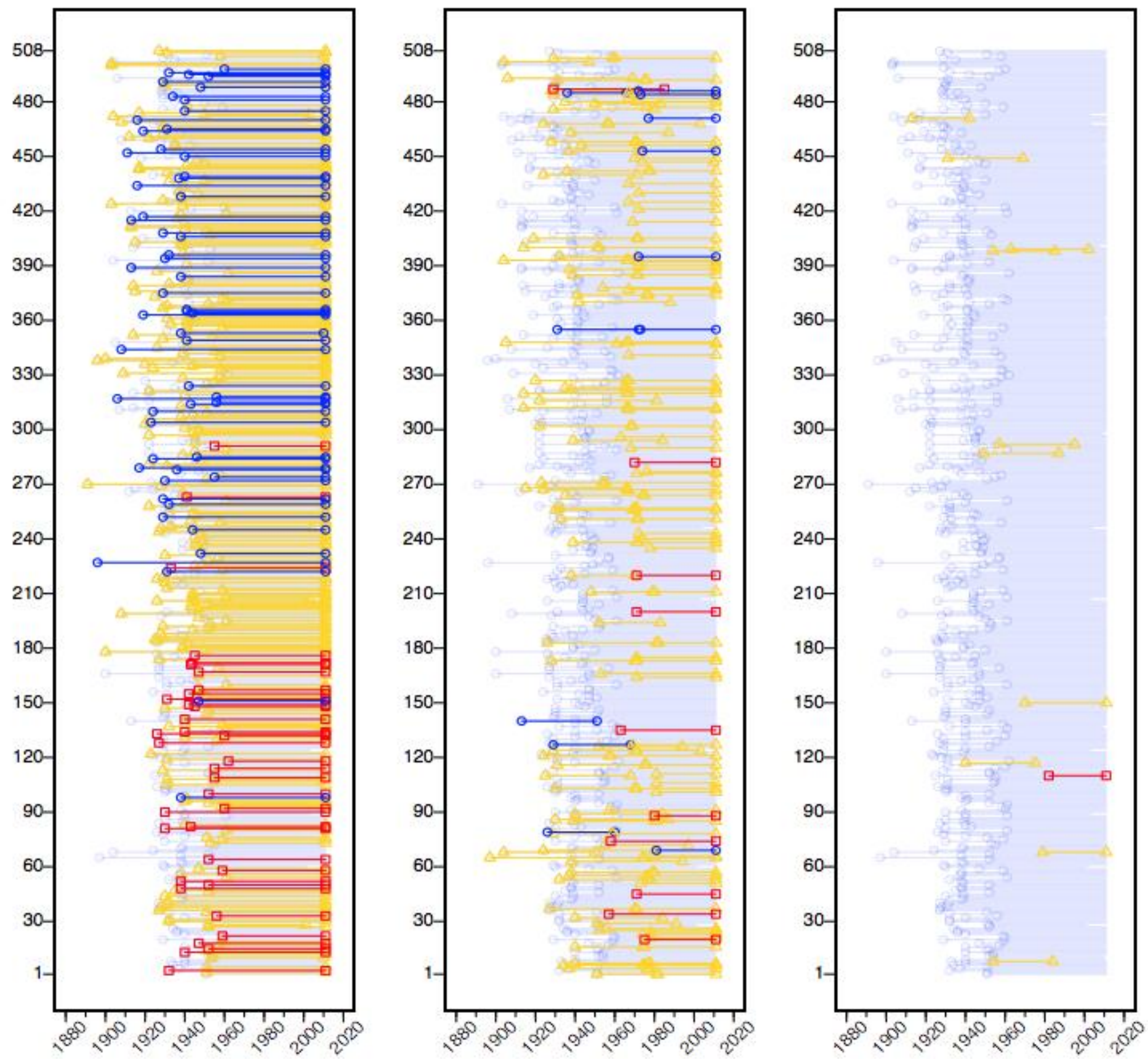


Figure 2. Range of years for each site which are stationary (trend is zero shown by yellow lines), or have increasing (blue lines), or decreasing (red lines) trends. The horizontal axis is the years and the vertical axes are the site numbers. Sites are ranked from the most southerly to the most northerly. The left plot shows the range of years from Step 1 of the decomposition algorithm. The middle plot shows the range of useable sub-series that is identified in the second recursion of the algorithm. The right panel shows the same but for the third recursion. Light blue lines show the original length of the time series.

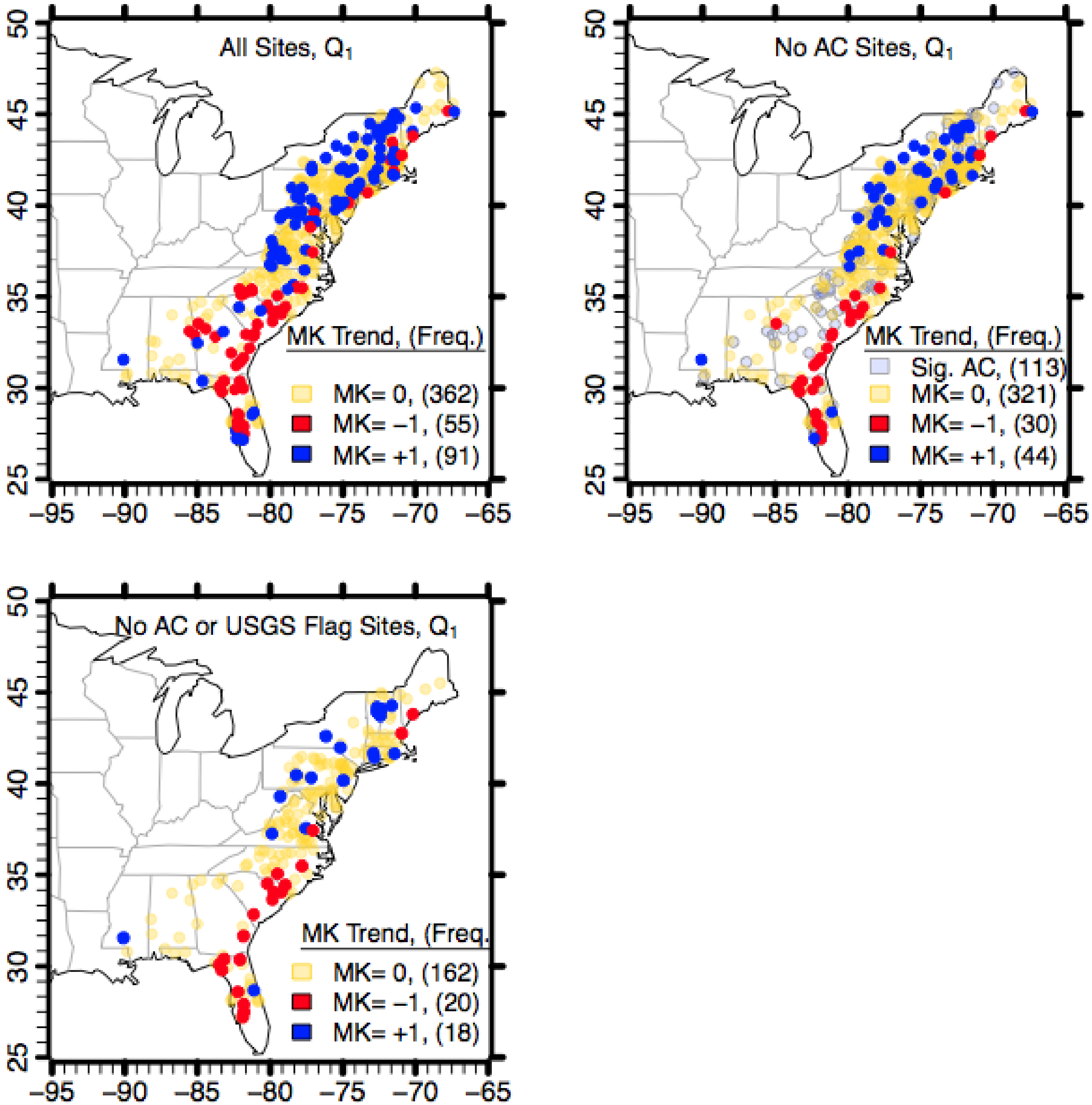


Figure 3. Trends in Q1 for 1951-2005 with and without consideration of autocorrelation and USGS flags. Top left: Mann-Kendall (MK) trend for all sites; Top right: MK trend with autocorrelated sites excluded; Bottom Left: MK trend with autocorrelated sites and USGS flagged sites excluded.

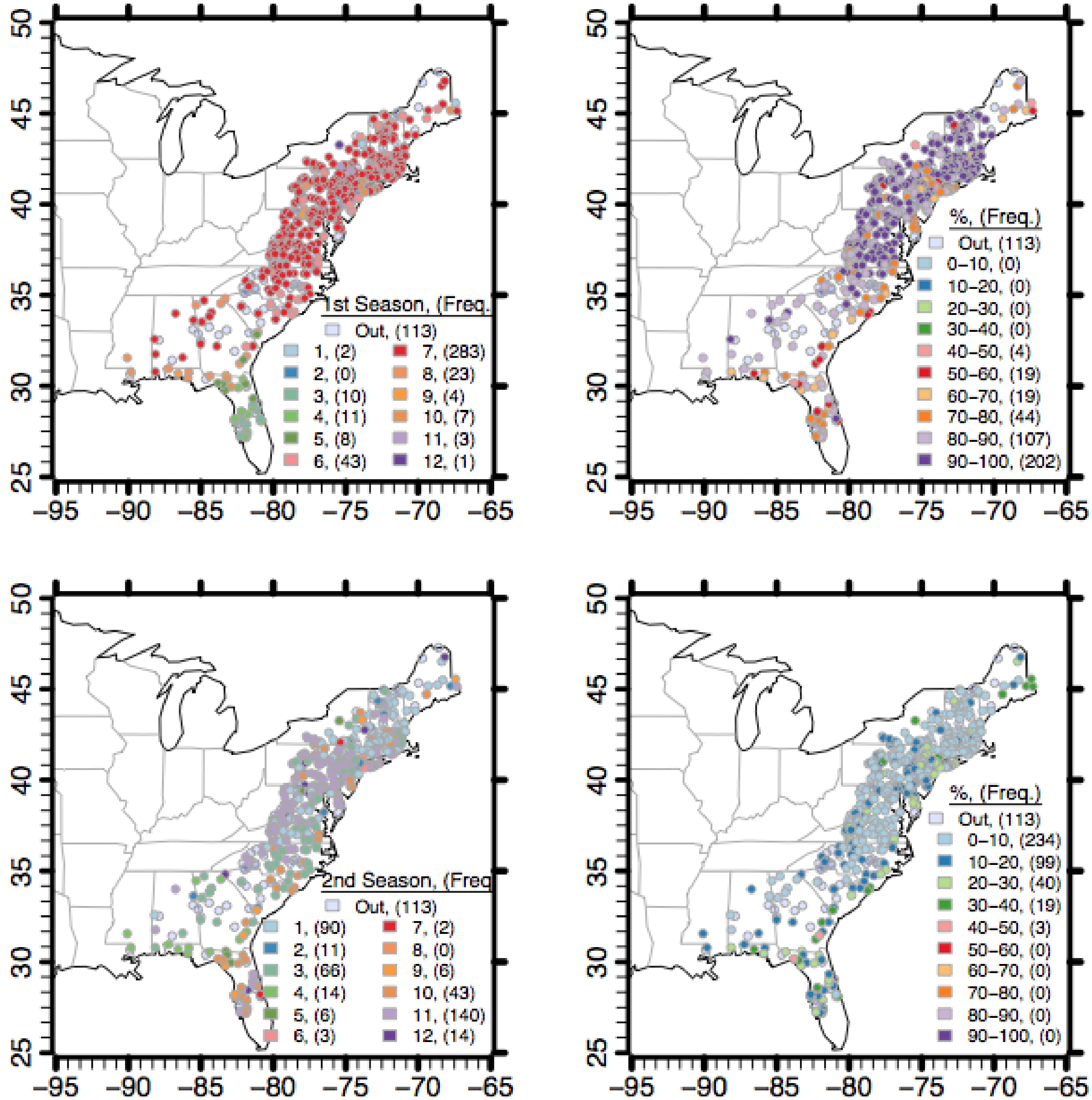


Figure 4. Date of occurrence of low flows for Q1. The top panels show (left) the starting month of the low flow season (1 is January and so on) and (right) the frequency of occurrence of low flow in that month. The lower panels show the same but for the second season of low flows.

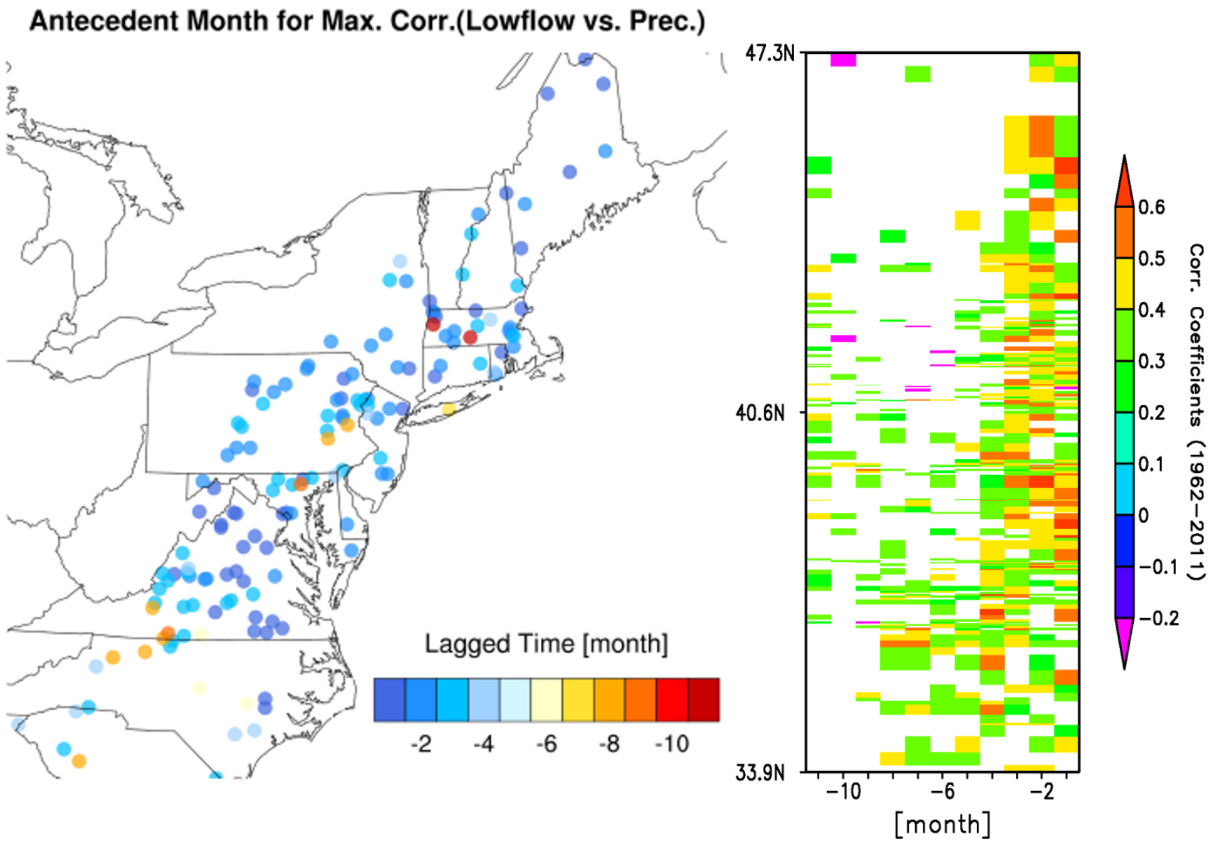


Figure 5. (left) Lagged time step with maximum correlation between annual 1-day low flows and annual monthly antecedent precipitation at one to ten lagged month time step from the date of annual 1-day low flow occurrences.

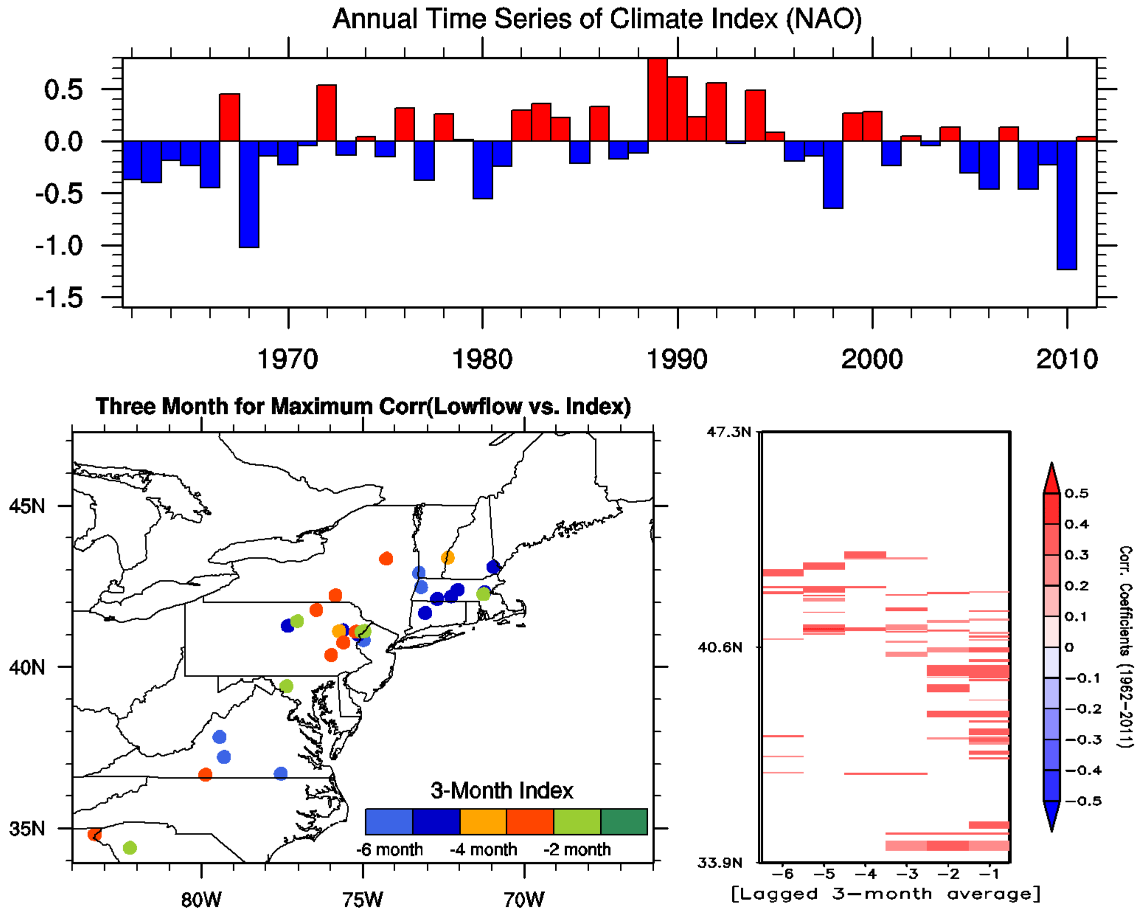


Figure 6. (top) Time series of annual North Atlantic Oscillation (NAO) index over 1962-2011. (bottom left) Lagged time step with maximum correlation between annual 1-day low flows and annual monthly antecedent precipitation. (bottom right) Temporal correlations between annual 1-day low flows and the antecedent precipitation at one to ten month lag time from the date of annual 1-day low flow occurrences.

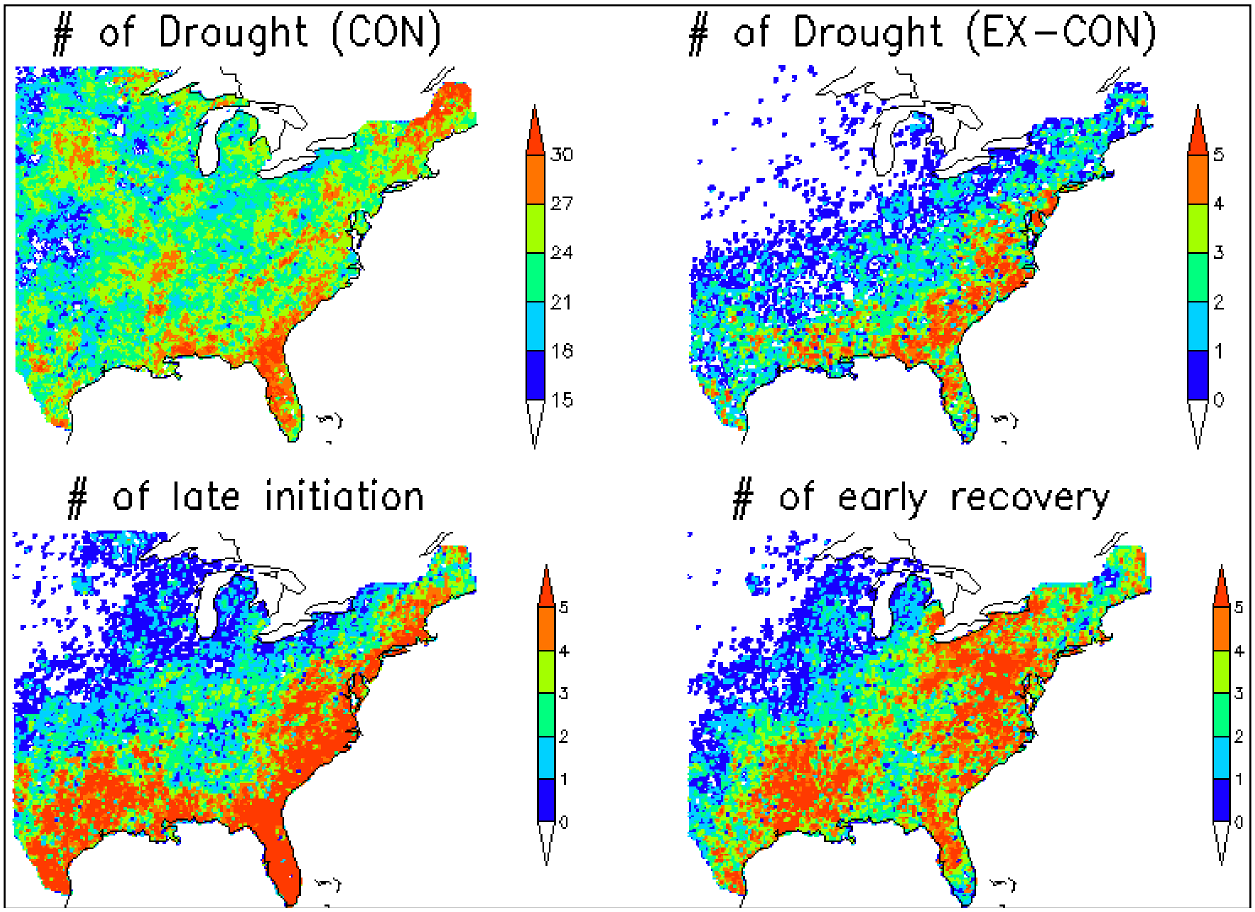


Figure 7. Total number of moderate severe and short-term drought events (top-left), the difference in number of droughts between the control and non-TC simulations (top-right; EX-CON), late drought initiation (bottom-left), and early drought recovery (bottom-right) during 1980-2007.

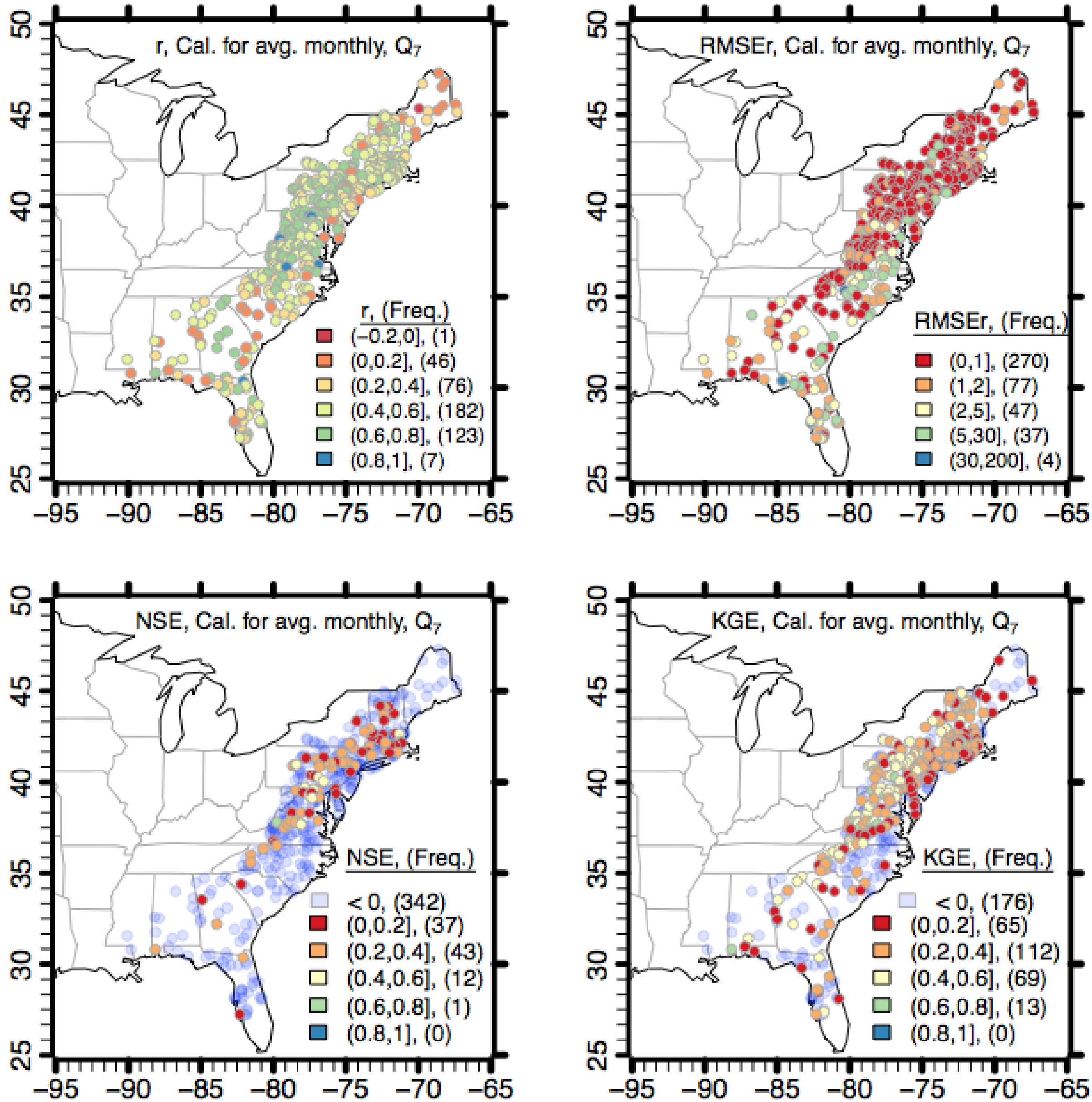


Figure 8. Performance statistics for the VIC model when evaluated against observed Q7 low flows at 408 USGS sites.

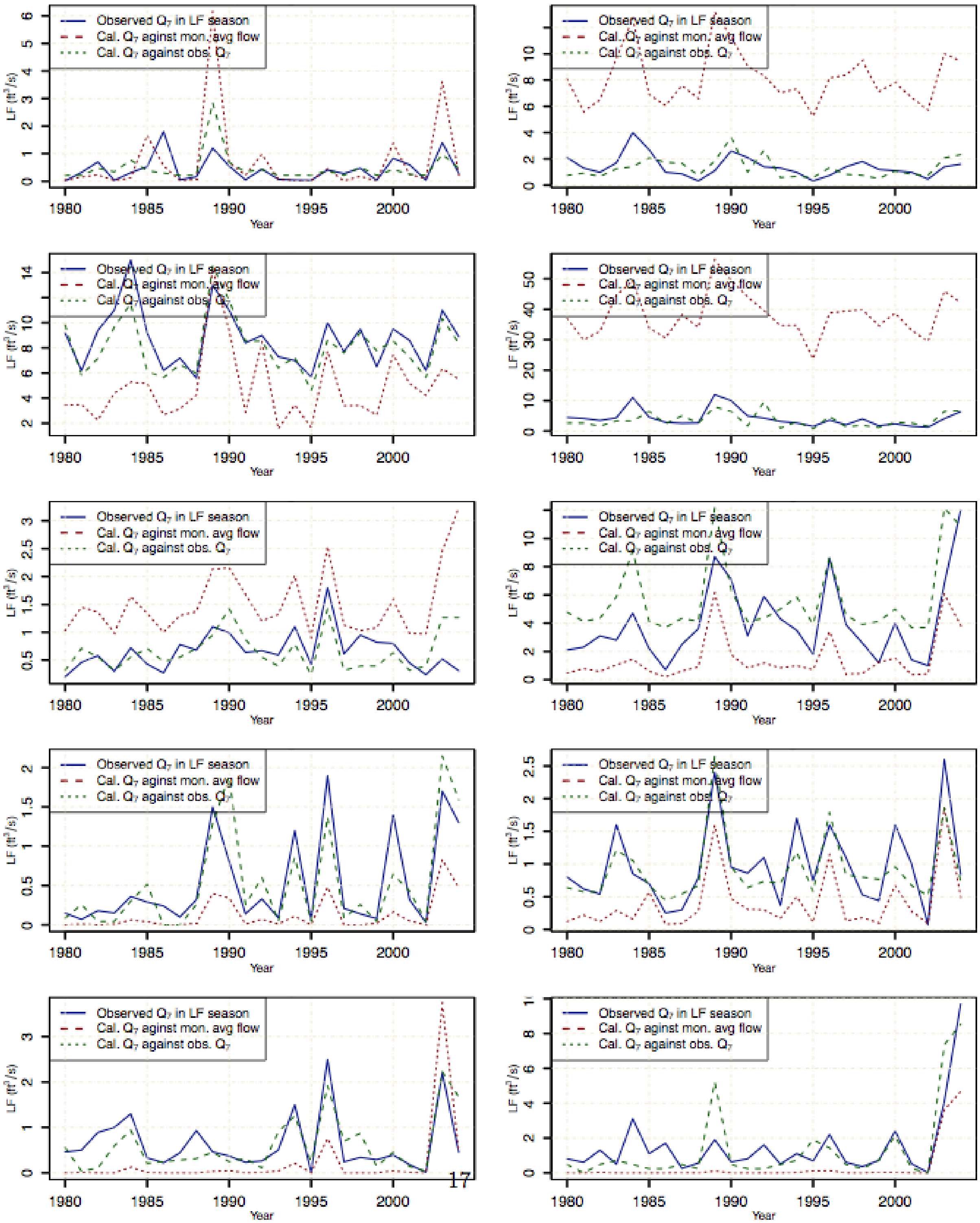


Figure 9. Comparison of VIC simulated Q7 low flows against USGS observations at 10 sites in the Northeast U.S. for the original monthly mean calibrated model and the Q7 low flow calibrated model.

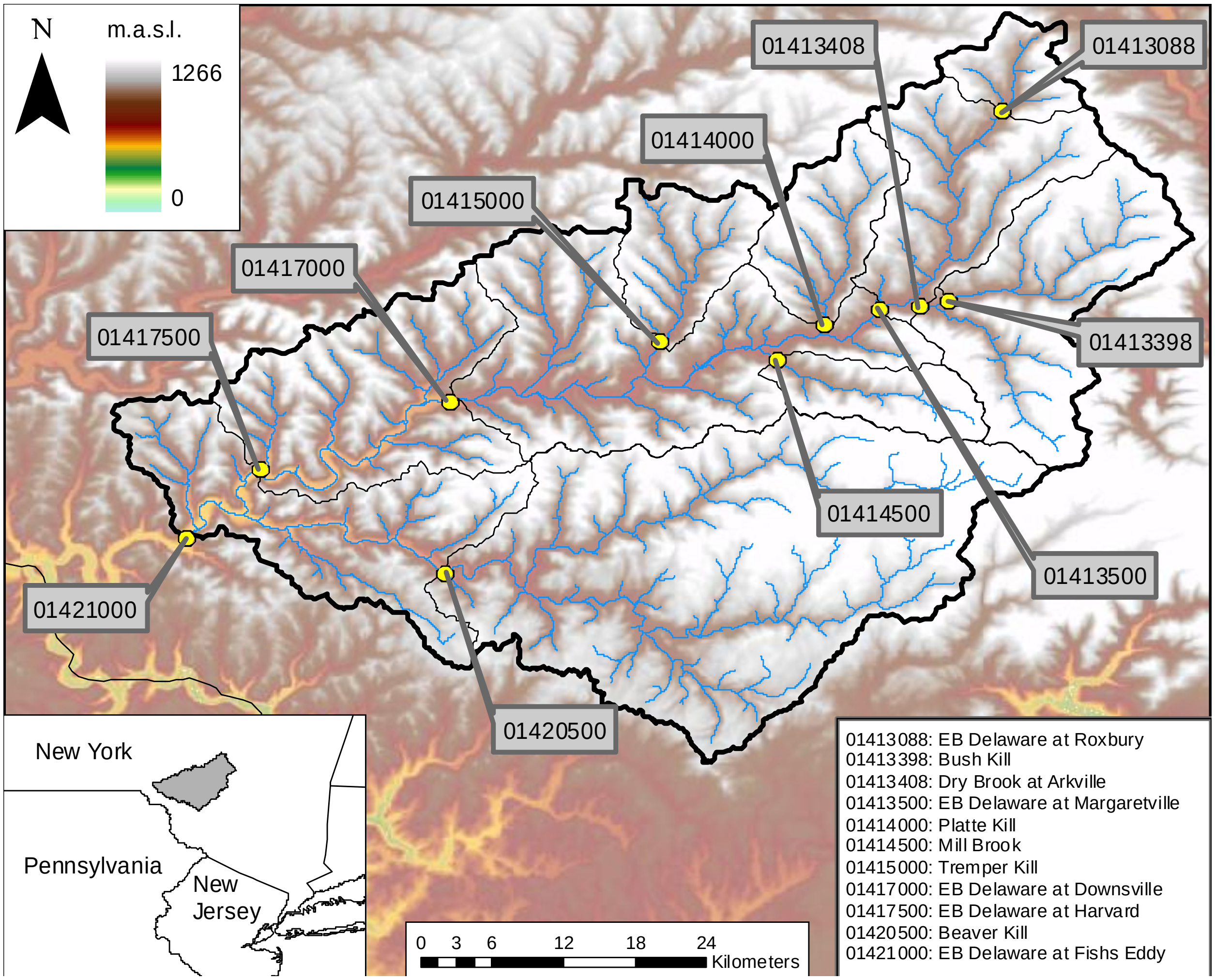


Figure 10. Location map for East Branch Delaware study watersheds, with USGS stream gaging locations.

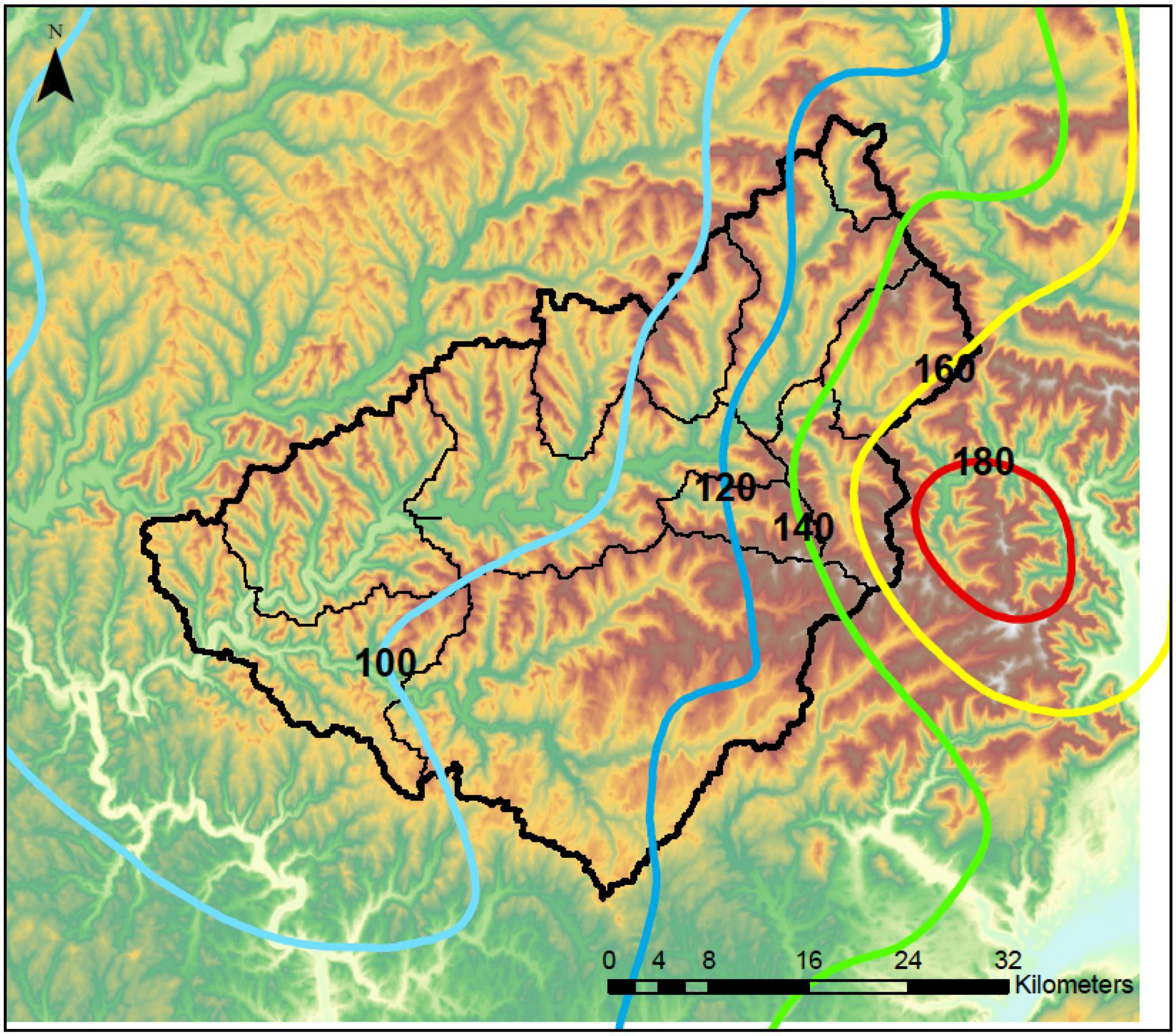


Figure 11. Storm total rainfall (mm) from Hurricane Irene (28-29 August 2011) based on bias-corrected Hydro-NEXRAD rainfall fields.

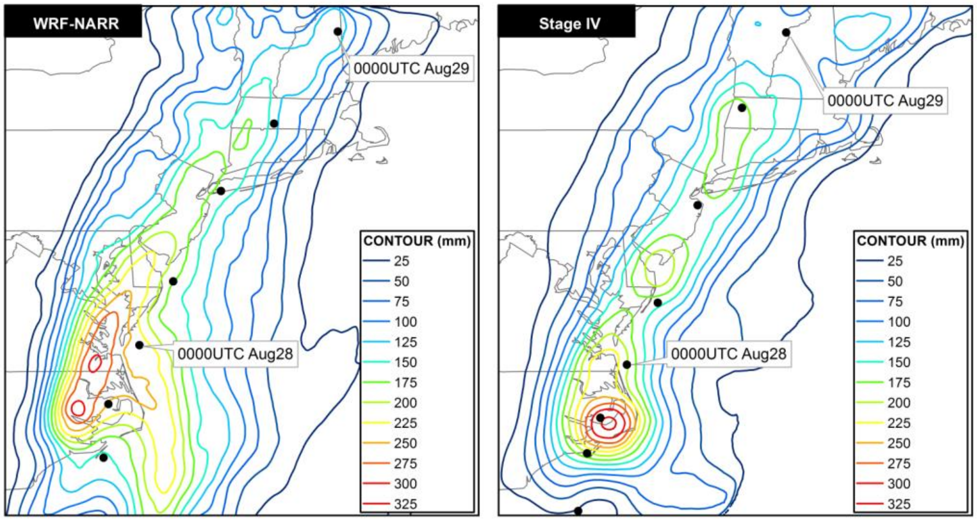


FIG. 12. Total storm rainfall (mm) of Irene from 0000 UTC 27 August to 0000 UTC 29 August. Locations of storm centers are indicated by black dots from WRF-NARR (3-hourly; left column) and best track data (6-hourly; right column).

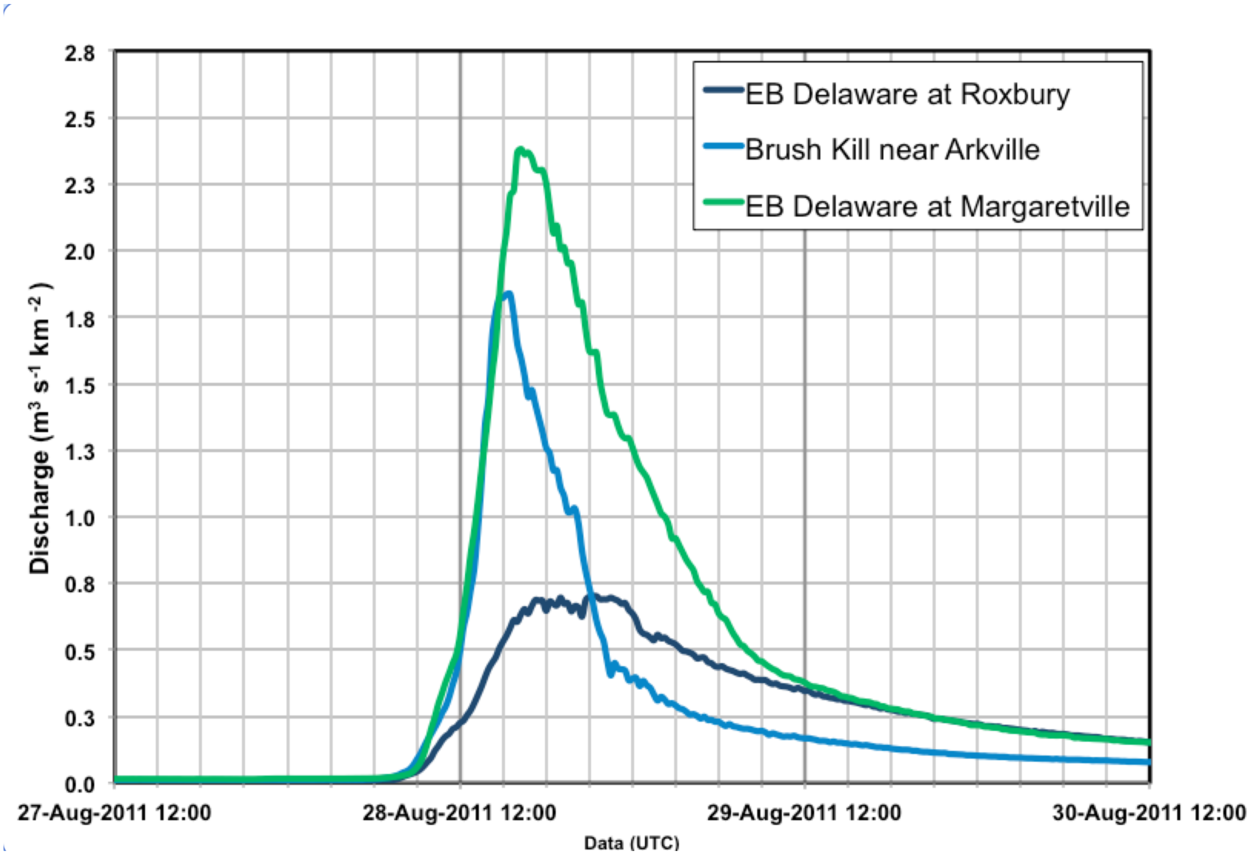


Figure 13. Discharge hydrographs (expressed as a unit discharge, i.e. discharge divided by drainage area) for Hurricane Irene in the East Branch Delaware at Margaretville (green), East Branch Delaware at Roxbury (black) and Bush Kill at Arkville (blue).

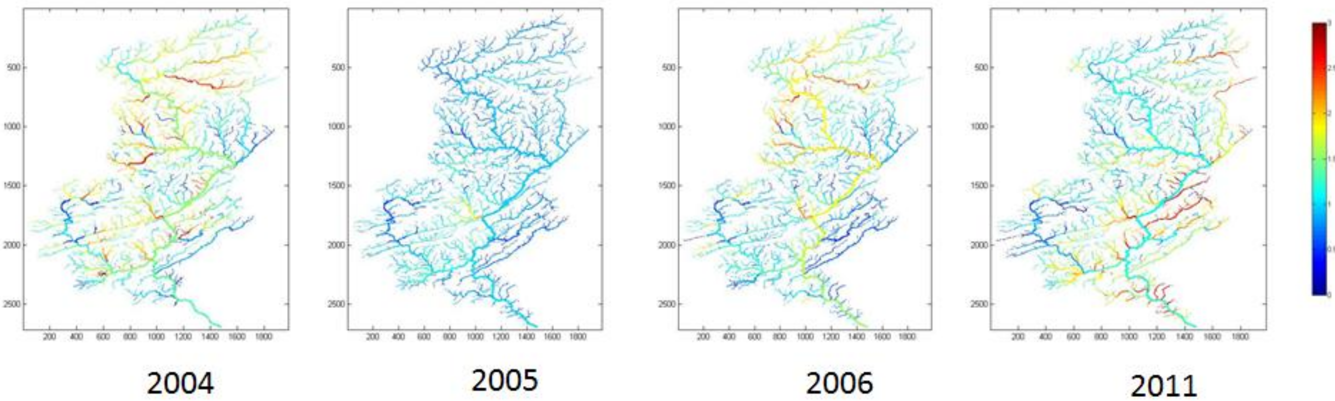


Figure 14. Flood index maps (peak discharge divided by 10 year flood) representing the distribution of flood magnitudes over the drainage network of the Delaware River basin for flood events in September 2004, April 2005, June 2006 and August 2011.

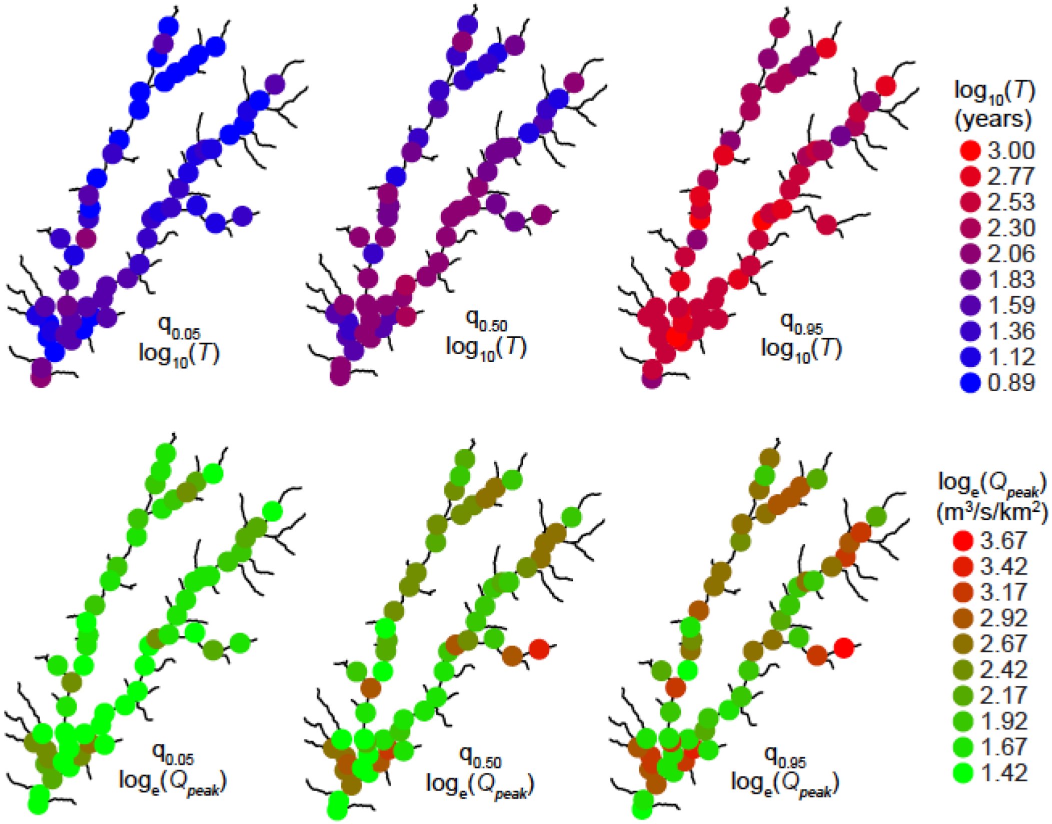


Figure 15. Spatial distribution of 0.05, 0.50, and 0.95 quantiles of return period T and area-normalized peak discharge Qpeak, estimated from the fifty events (one from each of fifty 1000-year SST realizations) that produced 100-year flood peaks at Little Sugar Creek at Archdale (Charlotte, NC).

Application of Graphene-based Sorbents for Arsenic and Lead Removal from Drinking Water Resources

Basic Information

Title:	Application of Graphene-based Sorbents for Arsenic and Lead Removal from Drinking Water Resources
Project Number:	2012NJ307B
Start Date:	3/1/2012
End Date:	7/31/2013
Funding Source:	104B
Congressional District:	NJ-008
Research Category:	Water Quality
Focus Category:	Toxic Substances, Treatment, Water Quality
Descriptors:	
Principal Investigators:	Shifeng Hou, Huan Feng

Publications

There are no publications.

Project Summary:

Problem and Research Objectives

This project utilizes graphene as an environment treatment agent to develop chemically modified graphene with high capacity and activity as sorbents for removal of heavy metals.

The proposed approaches are to fabricate and synthesize graphene with special functional chelating groups.

The goal of this project is to make graphene into high capacity, wide-spectra, re-useable, and lower cost sorbents that are a new generation of graphene-based nanoparticle sorbents.

The objectives of this research include:

1) Designing surface groups of graphene oxide with chemical modification techniques;

2) Utilizing surface groups as chelating groups to remove heavy pollutants;

3) Utilizing hydrophobic domains of graphene for organic pollutant removal;

4) Optimizing various operating conditions to control the adsorption capacity and activity;

5) Synthesizing magnetic nanoparticles on graphene surface for actual environmental application;

6) Investigating the complexing mechanism and adsorption kinetics between the functional groups on the graphene surface and heavy metal cations and organic pollutants using synchrotron X-ray and synchrotron infrared spectroscopy techniques.

Methodology

<u>The method includes</u>

(1) <u>New derivatives of GO</u>:

- Introduce functional groups onto the GO surfaces for arsenic removal.
- $-PO_3^-$, $-SO_3^-$, $-NH_2$ and $-SH$ are linked to GO surface through covalent reaction.
- Silanization is applied to introduce various functional groups onto GO surfaces.
- N-(Trimethoxysilylpropyl)-ethylenediamine, triacetic acid (EDTA-silane) and 3-Tri-methoxysilyl-propyl-diethylenetriamine (Amine-silane) are used first, and 3-trihydroxysilyl 1-propanesulfonic acid and 3-trihydroxysilyl 1-proppylmethylphosponate are synthesized and these materials are investigated now.

(2) **<u>Analytical methods:</u>**

Analytical tools such as FTIR, UV-vis, XRD, TEM, SEM and AFM will be utilized to monitor the synthetic process and to characterize as-obtained compounds. The test of zeta potential and elements analysis will be used to analyze the density of surface functional groups and thus evaluate its adsorption properties.

(3) **<u>Determine the physicochemical properties of the GO and FGO:</u>**

Zeta potential, the point of zero charge (PZC), and the concentration of acidic and basic sites on sorbent surface will be tested and evaluated.

(4) **<u>The adsorption mechanism</u>**

(5) **<u>Sorption Kinetics</u>**

(6) **<u>The effects of pH, the ionic strength, and the temperature on the adsorption properties</u>**
(7) **<u>Desorption Properties</u>**

Principal Findings and Significance

Our initial research approaches include (1) designing the GO surface with specific functional groups, and (2) investigating the adsorption mechanism and kinetics for As, Ni(II) , Cu(II) and Pb removal. We investigated the chemical and physical characteristics of functionalized GO; the interaction between toxic metals and the functional groups on GO and the effect of the GO structure on the adsorption capacities; and the adsorption kinetics and mechanism, and the renewable properties of GO-based sorbents.

The achievements thus far are listed below.

We synthesized new materials and investigated their potential application for Ni(II) and Cu(II) removal.

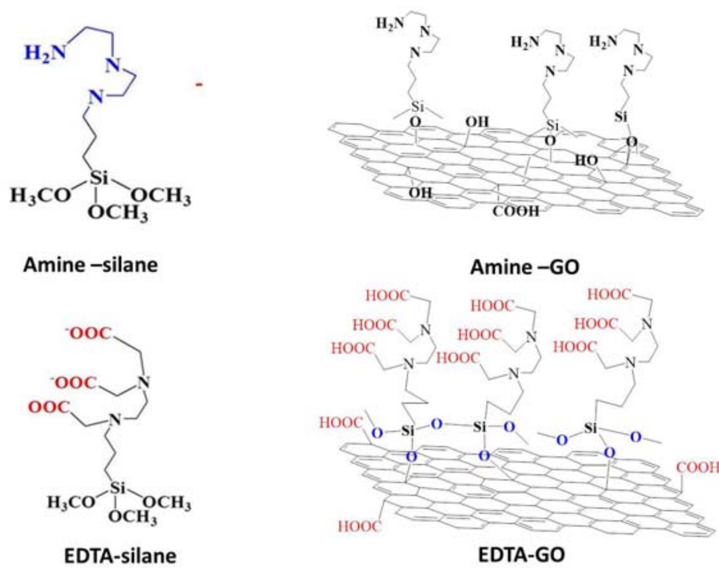
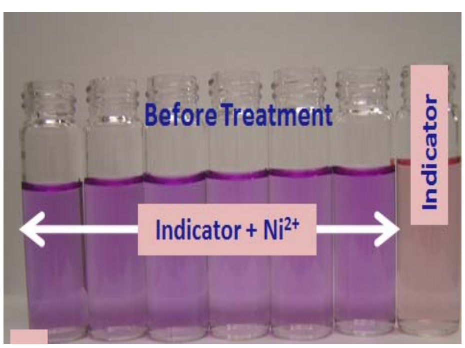


Figure 1. The chemical structure of Amine-GO and EDTA-GO.



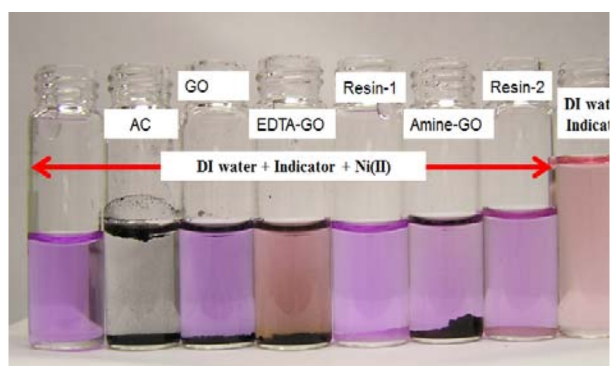


Figure 2. Various sorbent treated Ni (II) solutions.

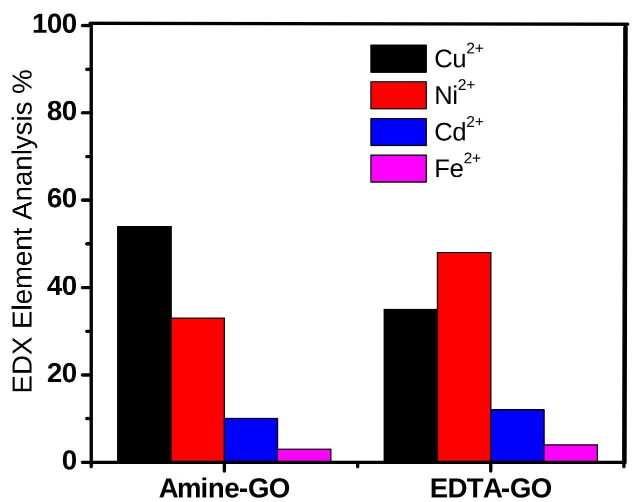
The adsorption behavior of Ni (II) on EDTA-GO fits the Langmuir equation well. The maximum adsorption capacities of EDTA-GO and amine-GO for Ni (II) are 103 mg/g and 86 mg/g, respectively, which are higher than that of GO, AC and other commercial products. The adsorption capacity varies with the pH value of the solution and these sorbents can be reused after washing with HCl. The simulation sample tests for Ni (II) removal demonstrate that at the same concentration level, 48% removed metals are Ni (II) at EDTA-GO. This research demonstrates that EDTA-GO can be a very effective sorbent for heavy metal removal and can be used to design some commercial products.

❖ It was found when four metal ions were co-existed at the same concentration, the percentage of Ni (II) on EDTA-GO surface (48%) was higher than all of the other three ions, which proved that EDTA-GO was a good sorbent for Ni (II) removal in a mixture solution.

❖ The percentage of Cu (II) on Amine-GO surface (52%) was higher than all other three ions, predicting that Amine-GO could be a good sorbent for Cu (II) removal in mixture solution.

❖ The above results suggested that GO modified with different functional groups could be designed for different heavy metal removal. Therefore, GO sorbent may provide selective separation of different metals from various waste water systems.

❖ The above materials to remove Arsenic are in progress. A final report with complete analysis will be provided in the near future.



❖

Figure 3. The EDXS element analysis of heavy metals on EDTA-GO and Amine-GO surface. Initial concentrations of Cu^{2+}, Ni^{2+}, Fe^{2+} and Cd^{2+} were 50 ppm respectively, sample dose was 20 mg/20 mL, and temperature was 25 ℃.

Predicting the matric potential of unsaturated porous media using nuclear magnetic resonance

Basic Information

Title:	Predicting the matric potential of unsaturated porous media using nuclear magnetic resonance
Project Number:	2012NJ309B
Start Date:	3/1/2012
End Date:	5/31/2013
Funding Source:	104B
Congressional District:	NJ-010
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Hydrology, Methods
Descriptors:	
Principal Investigators:	Sam Falzone, Kristina Keating

Publications

1. Falzone, S. and Kristina Keating. 2012. Laboratory measurements to explore the link between surface area, surface relaxivity, and NMR relaxation time in partially water saturation porous media. SEG-AGU Hydrogeophysics Workshop, Boise, ID. (poster presentation)
2. Falzone, S. and Kristina Keating. 2012. Laboratory measurements to explore the link between surface area, surface relaxivity, and NMR relaxation time in partially water saturation porous media. SEG-AGU Hydrogeophysics Workshop, Boise, ID. (poster presentation)

(1) Project Summary:

Problem and Research Objective

NMR is a unique geophysical method because it can directly detect water present within a sample volume (Dunn et al., 2002). NMR relaxation time, or the time by which the measured signal decays, is influenced by the distribution of water within the pore structure of soils, allowing the surface-area-to-volume ratio, *S/V*, of the sample to be determined in saturated samples (Brownstein and Tarr, 1979). Relaxation time is also affected by the paramagnetic content (i.e. iron (III)) of a sample, which directly effects the surface relaxivity, ρ_2, or the ability of the solid surface to enhance relaxation (Brownstein and Tarr, 1979). NMR measurements can be collected in the field, from the Earth's surface using surface NMR (SNMR) or in a borehole using logging instruments, and in the laboratory. Of interest in this research is developing NMR measurements that can be collected in the field using SNMR or in the laboratory to estimate the matric potential, ϕ_{Matric}. The research outlined in this proposal is designed to test the following hypothesis: *NMR relaxation times can be used to determine matric potential*.

Two laboratory experiments and a field study have been designed to test the hypothesis. The first laboratory experiment will explore the effects of *S/V* and ρ_2 on the relationship between saturation and NMR relaxation time. The second laboratory experiment is designed to develop an empirical relationship between NMR relaxation time, ϕ_{Matric} and saturation. In the field study, SNMR measurements will be made during an infiltration experiment and used to determine changes in saturation and ϕ_{Matric} over time. The results of this study will form a basis for developing methods for determining ϕ_{Matric} on a field scale using SNMR. Ultimately, the conclusions reached in this study will provide the scientists with a better way of determining ϕ_{Matric} in the vadose zone, which in turn will allow better monitoring of contaminants.

Methodology

Nine sands were used to study the relative surface relaxation, T_{2S}, versus saturation curves of samples varying in both ρ_2 and *S/V*. *S/V* was calculated from the specific surface area, measured with multi-point nitrogen BET absorption, and the porosity of the samples, determined gravimetrically. The value of ρ_2 were calculated from the *S/V* and T_{2ML} measured from saturated sample using laboratory NMR measurements.

The relative T_{2S} versus saturation curves were created by measuring the NMR response as deionized water was pumped into each sand. T_{2S} was calculated by subtracting the inverse bulk relaxation, or the relaxation time of DI water, from the inverse T_{2ML} for each sand. T_{2S} and A_0, which will be used to calculate saturation, were determined from NMR measurements collected every thirty minutes during both imbibition of DI water. The plots of T_{2S} versus saturation from each sand were compared to evaluate the individual effects of *S/V* and ρ_2.

Principle Findings and Significance

` The proposal to NJWRRI outlined three phases for the research covered in this proposal. Of these three phases, the first phase, outlined in the methodology above, has been completed. Several presentations have been given at conferncces concerning this research, and a manuscript has been submitted to Vadose Zone Journal presenting the key findings of this experiment. Of the remaining two phases, work is ongoing. All supporting equipment has been purchased and assembled. Data acquisition for the second phase will begin within the next two months. The data for the third phase has been collected, and is currently undergoing analysis. These findings will be prepared for submission to leading journals in the field of Geophysics and Soil Science, and will also be presented at relevant conferences, such as AGU 2013.

Comparing the Time Required for Establishment of Effective Nutrient Removal Capacity of Different Stormwater Basin Desgins

Basic Information

Title:	Comparing the Time Required for Establishment of Effective Nutrient Removal Capacity of Different Stormwater Basin Designs
Project Number:	2013NJ336B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-004
Research Category:	Water Quality
Focus Category:	Nutrients, Non Point Pollution, Water Quality
Descriptors:	
Principal Investigators:	Theresa Censoplano, Louise Wootton

Publications

There are no publications.

(3) **Project Summary**:

A solution to dealing with excessive quantities of phosphorous and nitrogen in the Barnegat Bay lies in limiting the amount of nutrients that make their way into aquatic ecosystems (Dietz and Clausen 2005). One approach is the use of subsurface gravel wetlands (SSGW), which allows a decrease in water flow and filtration as water flows horizontally through a wetland system promoting the conversion of nitrogen fertilizer chemicals to harmless N_2 gas. This study will test the effectiveness of nutrient removal of four different designs of subsurface gravel wetlands, with a focus on nitrogen pollution reduction. The four wetlands to be tested are: a wetland built on the original University of New Hampshire Stormwater Center (UNHSC) subsurface gravel wetland design, two modified UNHSC designs, one of which contains a simplified plumbing design and the other a deeper gravel layer and an Advanced Bioretention System. Water collected in a central well from a large parking lot at Georgian Court University will be split into equal flows that will feed the four test wetlands. Water samples will be collected during major rain events from the central well, as well as from each wetland outlet and tested for ammonia, total Kjeldahl N, nitrate, nitrite, total N, total P and orthophosphate. Nutrient removal efficiency will be determined through comparisons of inlet and outlet nutrient concentrations of each test wetland. The resulting information will be used to inform development of best management practices for stormwater design.

Methodology - give a general summary of procedures and methods actually implemented

Due to construction delays, the procedures and methods that will be used to obtain nutrient concentrations has not yet begun. Construction on the gravel wetlands is scheduled to begin the week of May 19, 2014. I expect to collect the first set of samples in early July, dependent on rainfall, and to sample approximately monthly thereafter.

Principal Findings and Significance - N/A project not yet started

Detoxification of dioxins in sewers

Basic Information

Title:	Detoxification of dioxins in sewers
Project Number:	2013NJ337B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-006
Research Category:	Water Quality
Focus Category:	Acid Deposition, Toxic Substances, Treatment
Descriptors:	
Principal Investigators:	Yashika Dewani, Lisa A. Rodenburg

Publication

1. Dewani, Yashika; Amy Deighan; Lisa Rodenburg. 2014. Using CARP Data to Investigate the Dechlorination of Dioxins in the NY/NJ Harbor Watershed . Poster Presentation. 99th Annual New Jersey Water Environment Association Conference. Atlantic City, New Jersey.

(4) **Project Summary**:

Problem and Research Objectives:

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), especially the most toxic congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), are a problem in the New York-New Jersey Harbor. The Health of the Harbor Report notes that dioxin concentrations found in estuary sediments were above EPA Guidance Value from approximately 1950 to 1980 in the Newark Bay and Lower Passaic Regions. The same was discovered of the NY/NJ Harbor Region from 1950 to 1990. [1] Since sewers, especially the combined sewers prevalent in the New York City area, aggregate pollution from many sources, they build up high levels of dioxins, which can then be flushed into receiving water during storm events. If the bacteria in sewers are able to detoxify the dioxins, then they can prevent dioxin contamination from reaching the waters of the NY/NJ Harbor.

PCDD/Fs are highly persistent. Virtually the only pathway by which they can be degraded is via dechlorination by anaerobic bacteria. Although studies on the microbial reductive dechlorination of PCDD/Fs have been reported, published dechlorination rates range over several orders of magnitude because of the difficulty and expense of sample preparation and analysis. In general, however, dechlorination of PCDD/Fs is often too slow in contaminated sediments to significantly impact environmental concentrations of PCDD/Fs. Ideally, for effective bioremediation to occur in an area with an abundance of PCDD/Fs, faster dechlorination is desired. Microbial dechlorination of PCDD/Fs can follow either the *peri*-dechlorination pathway, which removes chlorines at the 1, 4, 6, and 9 positions, producing 2,3,7,8-substituted products, or the *peri*-lateral pathway that also removes chlorines at the 2, 3, 7, and8 positions, resulting in the production of non-toxic congeners that are not 2,3,7,8-substituted.[2-5] For this reason, PCDD/F dechlorination is easier to detect when all of the 210 PCDD/F congeners are measured. Unfortunately, many data sets, including the Contamination Assessment and Reduction Project (CARP) data, only measured the 17 2,3,7,8-substituted congeners. However, during the analyses of these 17 congeners, data is also generated to measure other non-2,3,7,8-substituted congeners that could be products of dechlorination. This research will utilize the raw chromatograms from the original CARP data to quantify the non-2,3,7,8-substituted congeners in many of the CARP samples. This is far less expensive that collecting new data.

Recently, our research group published evidence that polychlorinated biphenyls (PCBs) are extensively dechlorinated in sewers and landfills.[6] PCDD/Fs are structurally similar to PCBs in that they both contain aromatic chlorines, suggesting that PCDD/Fs are dechlorinated in sewers and landfills along with PCBs. Three other studies indicate that bacterial strains that are capable of dechlorinating PCBs can also dechlorinate PCDD/Fs.[8-10] Sewers and landfills are ideal environments where anaerobic bacteria and thrive and utilize chlorinated compounds as electron acceptors. To investigate the possibility that PCDD/Fs are also dechlorinated in sewers, the Contamination Assessment and Reduction Project (CARP) provided us with a data set in which both PCBs and the 17 2,3,7,8-substituted PCDD/Fs were measured in WWTP influent and effluent. [7] Here, only the products of the *peri*-dechlorination pathway were measured. Using this data, we found evidence that PCDD/Fs are dechlorinated in sewers via the *peri*-dechlorination pathway. [11] Thus, the goal of the proposed research was to further this investigation by adding the non-2,3,7,8-substituted congeners into our data set, allowing us to look for the non-toxic *peri*-lateral dechlorination products and to determine whether *peri*-lateral dechlorination of PCDD/Fs occurs in sewers, landfills, and harbor sediments in the NY/NJ Harbor watershed. The central hypothesis of this work is that PCDD/Fs are dechlorinated in sewers and landfills along with PCBs.

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Methodology:

1. Obtaining data packages and transcribing them into Excel

The original PCDD/F chromatograms for the CARP analyses were obtained from Axys Analytical Services. These chromatograms contained information on the concentrations of both the 2,3,7,8-substituted and the non-2,3,7,8-substituted PCDD/F congeners with four to eight chlorines. The calculated concentrations of these congeners were provided on the chromatogram. These sample packages, which are now over 10 years old, were presented in the form of pdf files that were scanned from printouts that contained hand-written notes. Because of this, data packages could not be exported directly onto a spreadsheet, nor could optical character recognition be used on them. Thus, the information from these packages were transcribed manually into an Excel spreadsheet and combined with the existing CARP data available on the CARP CDs. [5] Data was checked to ensure that any concentration information met data quality criteria, including the correct ratio of quantifying and confirming ion abundances and detection limits (these were also provided in the data packages provided by Axys).

2. Comparing to MS Access Database

In order to ensure accuracy, the octachlorodioxin (OCDD) concentrations provided in the original chromatograms were checked alongside their corresponding values provided in the CARP Microsoft Access database. The resulting spreadsheet of sample concentrations was organized into several different categories. Furans and dioxins were separated from each other, which were then separated into congeners that were non-2,3,7,8-substituted and those which were 2,3,7,8-substituted. These were then separated further by homologues, and then by sample location class, which was indicated on the CARP database. The data were lumped together as follows: ambient water samples which include major tributaries (7 samples), minor tributaries (10 samples), and ambient non-kills (1 surface water sample); sludge (12 samples); water pollution control facility (treated effluent) (41 samples); storm water samples which include storm water overflows (2 samples), trackdown samples (usually collected in sewers) (2 samples), and combined sewer overflows (22 samples); and landfill samples which include landfill (9 samples) and indefinite samples (6 samples). The indefinite samples were combined with the landfill samples because their GPS coordinates indicated that they were obtained from the Fresh Kills landfill. These landfill sampling points were located around the landfill mounds, and the leachate was collected using a system of trenches and pumps. [10]

3. P/(P+L) percentages and SigmaPlot

The percentage of peri as opposed to lateral chlorines on a dioxin or furan can be an indicator of peri-lateral dechlorination. Dechlorination reactions result in the loss of mass, but not in total molar concentration. Therefore, reporting concentrations of congeners at various stages of dechlorination as molar percentages is preferable. [14] Furthermore, reporting results as percentages allows for focus on the changes in PCDD/F composition via dechlorination by neutralizing sample-specific properties, such as pollution level. [Sundqvist et al, 2009] The resulting value provides the percentage of 2,3,7,8-substituted PCDD/Fs in each sample set, thereby illustrating the likely dechlorination pathway of that compound within its particular sample location. Sample sets with lower percentage values imply a higher yield of non-toxic products, with fewer chlorines in the lateral positions. Because the peri-dechlorination pathway has been studied before, comparisons of the results can be made alongside values in existing literature.

The concentrations for each analyte (with the exception of the sludge samples) were obtained by dividing by the sampled volume. Because the sludge samples were considered to be solids, they were divided by grams of dry weight per sample. To obtain the percentage of the non-2,3,7,8-substituted congeners within the sample location class for each homologue, the amount of non-2,3,7,8-substituted congeners was divided by the summation of all of the congeners (both 2,3,7,8- and non-2,3,7,8-substituted) in each case, as demonstrated by the following equation:

$$Percent\ peri = \frac{P}{P+L}$$

Here, the P symbolizes the sum of the concentration of the non-2,3,7,8-substituted congeners, whereas P+L refers to the total homologue concentration (peri plus lateral).

To examine whether the percent peris of peri-lateral dechlorination for each homologue location class were significantly different from each other, an unpaired two-sample students t-test was conducted using SigmaPlot. This program automatically conducted the preliminary f-test for each t-test to determine whether the comparable sample sets were of equal or unequal variance. P-value results less than or equal to 0.05 indicated a statistically significant difference between the two data sets.

4. Assembling spreadsheets for Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF) was then utilized on CARP data to attempt to examine whether *peri*-lateral dechlorination of PCDD/Fs occurs in sewers in the NY/NJ Harbor watershed and to determine the source factor locations of these potential occurrences. An Excel spreadsheet transcribed with the CARP data was assembled into an input file for PMF analysis. It should be noted that not all of the samples were used in the PMF matrix. Dissolved phase (XAD) samples were discarded from the data set because they always sorted out into their own separate factor. Furthermore, XAD would ideally be added to a corresponding filter, yet there was not always a corresponding filter which was available. Thus, it was assumed that any sample amount in the dissolved phase was negligible. Instead, all of the filter, whole water, and sludge samples were the ones that were utilized for PMF analysis.

In this particular type of analysis, multiple different types of permutations are run through the PMF model in the form of various matrices. Here, three matrices were assembled for our purposes: a concentration matrix, an uncertainty matrix, and an LOD (limit of detection) matrix. The concentration matrix consisted of mass concentrations of each PCDD/F congener within each sample obtained directly from the CARP data sheets which were provided to us on the CARP CDs. Typically for the concentration matrix, data points which are below detection limit (BDL) values are either replaced with one-half of the LOD, or they are multiplied by a random number centered around 100%. In order to assemble the LOD matrix, an average limit of detection is applied to each congener within every sample in the original base case matrix (the matrix assembled prior to any permutations and alterations). For the uncertainty matrix, an amount of uncertainty (0.15) was assigned to all detected concentrations, and a separate uncertainty (1.66) was prescribed for the below detection limit (BDL) values. This matrix was then modified by multiplying each detected value by its associated analytical surrogate recovery for each particular congener. In order to increase the difference between the detected and BDL concentrations, the BDL values in the uncertainty matrix were multiplied by three times the surrogate recovery value assigned for that homologue. RSD (relative standard deviation) values for the analytical surrogate recoveries of certain congeners were available to us, and they were assigned to acceptable and exchangeable congeners using Table 2 in EPA Method 1613. If one congener within a particular homologue was able to be assigned a particular RSD substitution value, then the entire homologue was assigned to this value. If a certain homologue could be matched up with more than one of these RSD values, the values were then averaged and subsequently applied to the entire homologue. In the case of the pentadioxin homologue where there was no available matching RSD value, a value of 0.25 was assigned because it was similar enough to the RSD substituted values of the other homologues, and it fell within the range of the other RSD values for the homologues (0.218675 to 0.39883).

2. Using PMF to generate factor (source) profiles

Initially, three matrices with dimensions of 135 rows by 84 columns were created, before duplicate samples were detected and eliminated. This resulted in matrices of a somewhat smaller dimension, 127 by 84, which was run through the PMF program. The seed number for each factor was 9, in order to ensure an uneven number of results in case if a "tiebreaker" was required when comparing differences amongst output values. However, the results in this particular PMF run displayed a great disparity amongst the output Q values amongst the individual factors and high overall relative standard deviation (RSD) factor values. Therefore, samples with unfavorable R^2 values (when comparing the correlation between the measured and the modeled concentrations for the samples) below 0.70 shared across all factors were removed. These samples were mainly obtained at WPCFs (1SPL02576 was collected at North River; 1SPL02761 and 1SPL02834 were from Newtown Creek; 1SPL02772, 1SPL02774, and 1SPL02869 were from Hunt's Point; 1SPL02773 and 1SPL02832 were from Port Richmond; and 1SPL02808 and 1SPL02809 were from 26th Ward), and one was a storm water sample (1SPL02995 was collected from the Manhattan Grit Chamber).

This resulted in a 116 by 84 set of input matrices, which was subsequently run through the PMF program again. The OCDD congener was then removed because its mass percentage was far too large for the data set, thereby skewing the results and leading to unusually low R^2 values. The 116 by 83 matrix was run through the PMF program and whittled down once more for greater accuracy. Four samples were excluded (1GRW05021 and 1GRW05125 were ambient samples from the Wallkill River in New Paltz, 1SPL02970 was a landfill sample obtained from 1D-HMDC, and 1SPL02984 was a storm water sample obtained from the Manhattan Grit Chamber). The 6 congeners with low R^2 values which were removed were 1,2,4,8,9/1,2,6,7,9/1,2,3,6,9-PeCDF; 1,2,3,4,9-PeCDF; 1,2,3,7/1,2,3,8-TCDD; 1,2,3,9-TCDD; 1,2,8,9-TCDD; and 1,2,4,6,8/1,2,4,7,9-PeCDD. Five factors were chosen for PMF analysis for these 112 by 77 matrices because any amount over this created an unacceptably high RSD for the data set.

Principal Findings and Significance:

Two out of the three laboratory samples with the highest TEQ values, and therefore the highest toxicity, were obtained from combined sewer overflow sampling locations (Figure 1). Some of the CSOs in the Passaic River basin are so low-lying that at high tide, water from the river backs up into them, explaining the high toxicity of the storm water samples from the Passaic River area. Therefore, if dechlorination of PCDD/Fs does indeed occur in sewers, it would be beneficial for detoxifying existing sediments within these particular sample locations.

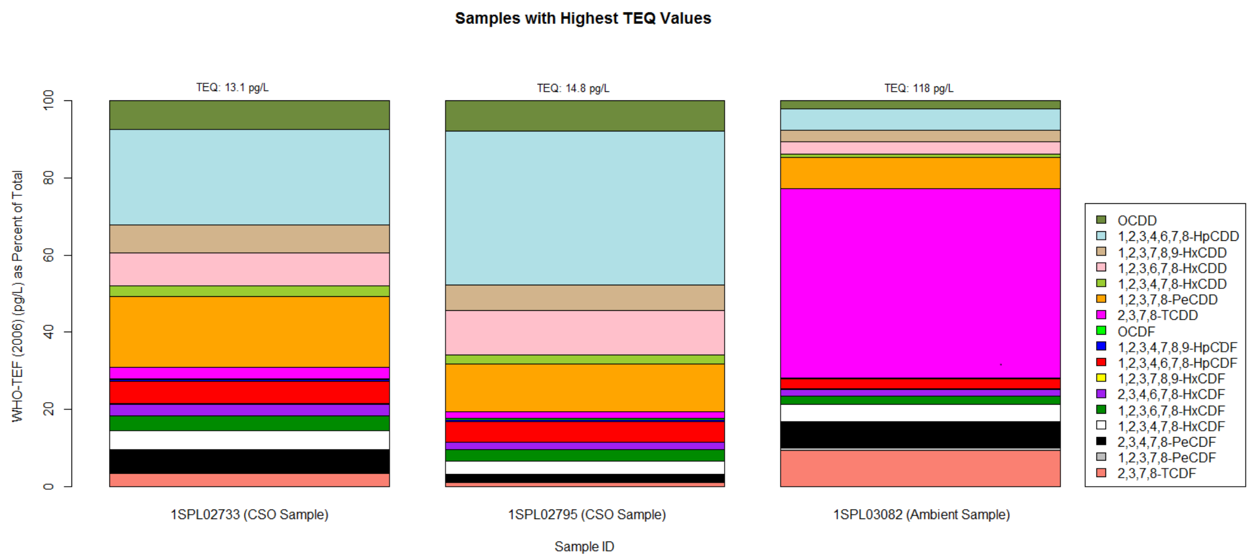

Figure 1. Three samples from data set with highest TEQ values. Toxicity contribution is examined by each individual PCDD/F homologue within each sample in terms of percent of total.

Within the original data set, the concentrations of non-2,3,7,8-PCDD/Fs were already far lower than those of the 2,3,7,8-PCDD/Fs, suggesting that perhaps a significant amount of peri-lateral dechlorination may not occur overall. However, it should be noted that we are not measuring for all of the products of dechlorination, since the mono- through tri- substituted PCDD/Fs were not provided within the CARP data set. Additionally, the greatest concentrations of non-2,3,7,8-PCDD/Fs in the data set were present within the storm water sample subset, which contained the CSO samples. Within the original non-2,3,7,8-substituted PCDD/F water sample subset, it appears that a general trend is present in which the most abundant congeners are increasingly present in higher chlorinated homologues (HpCDD/Fs congeners are greater than HxCDD/Fs, which are more abundant than PCDD/Fs, and so on). It should also be noted that a greater percentage of non-2,3,7,8 congeners were present within the PCDF samples than in the PCDD samples.

When examining the percent peris in the box-and-whisker plots (Figure 2 and 3), it appears that a general trend exists within the non-2,3,7,8-substituted PCDFs in which a greater amount of dechlorination occurs within storm water samples as the homologues become increasingly chlorinated. In particular, the results suggest that HxCDFs are best dechlorinated within sewers amongst the furan homologues. However, it appears that the opposite occurs within the PCDD homologues. Additionally, it appears that there is greater actual difference between sample subclasses within the dioxins than in the furan subset (Figures 4 and 5).

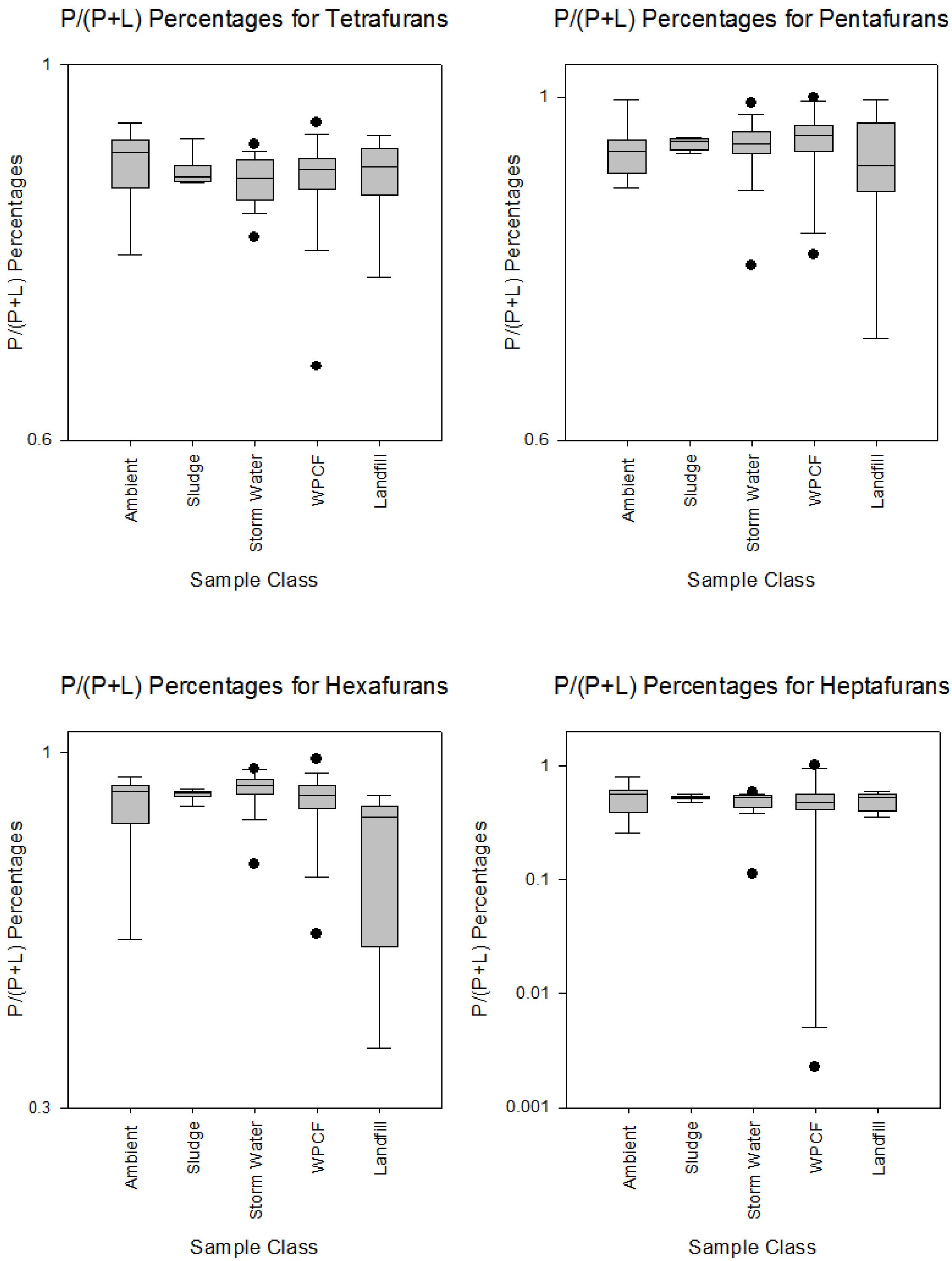

Figure 2. Percent Peris for PCDF homologues.

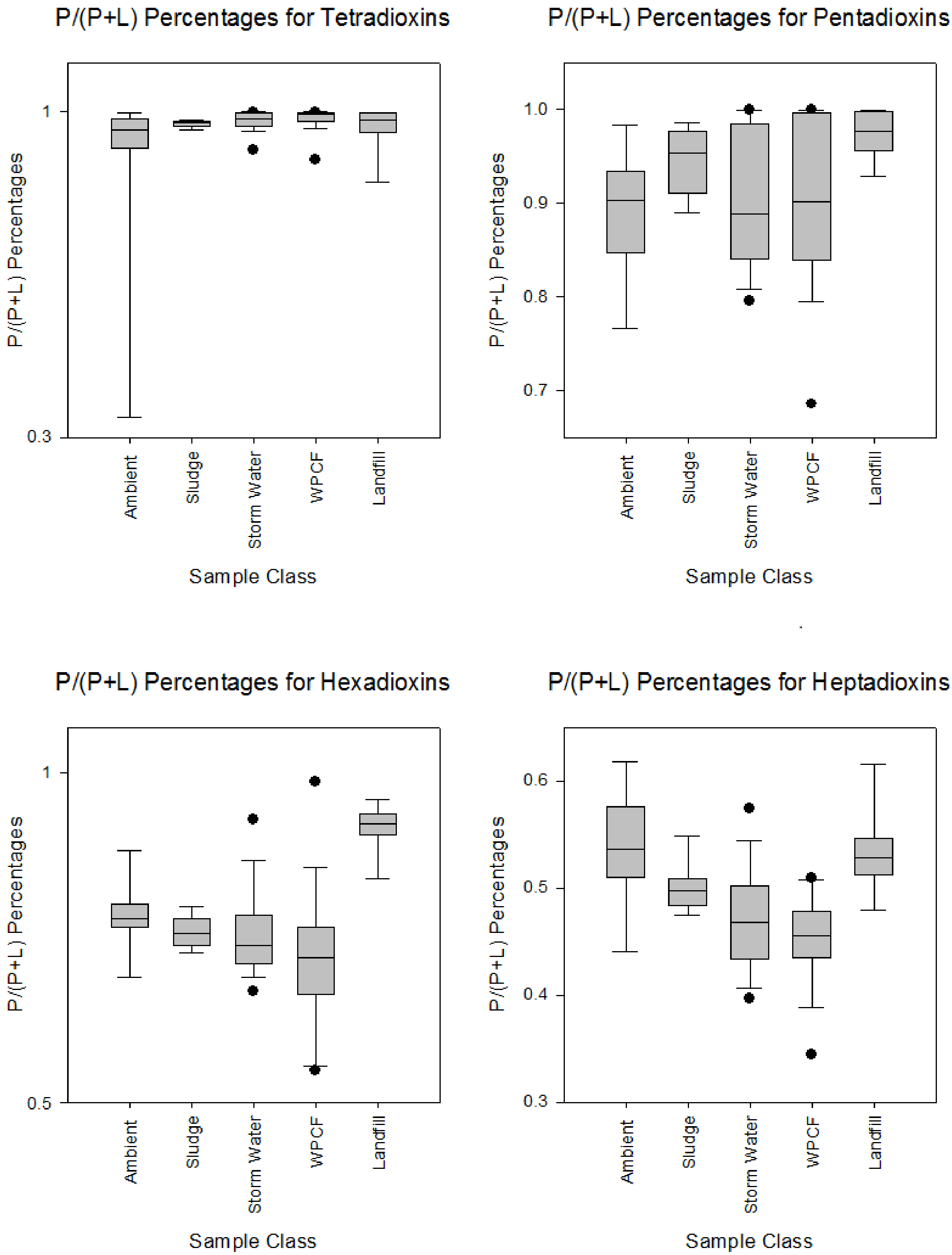

Figure 3. Percent Peris for PCDD homologues.

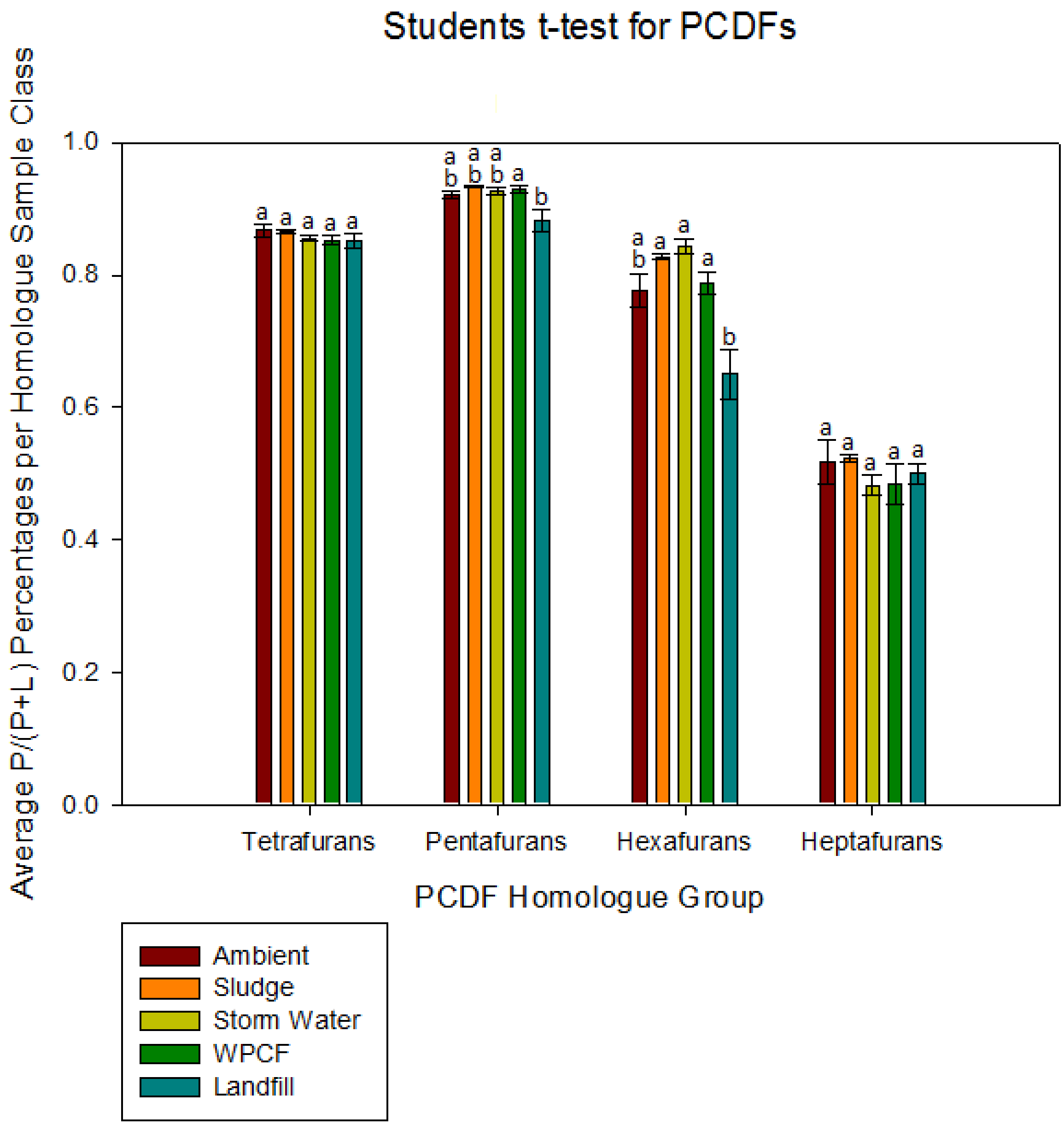

Figure 4. Students t-test for PCDF homologues. Average percent peris for each sample class are plotted, and 95% confidence interval error bars are displayed. Bars with letters differing from each other within each homologue group indicate a difference between sample classes due to p values of <0.05.

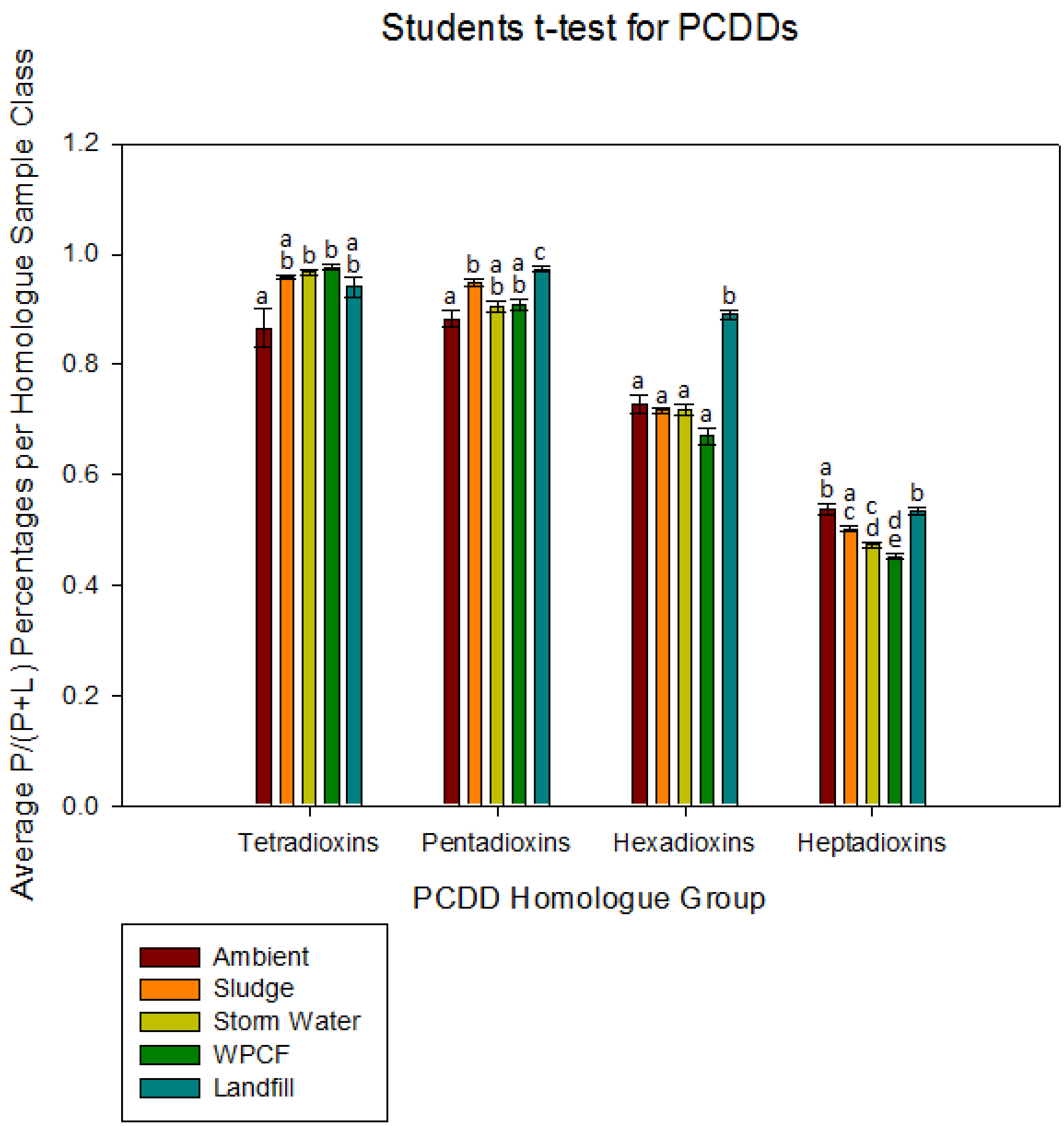

Figure 5. Students t-test for PCDD homologues.

This project is in its final stages yet it will be continued in order to provide a better interpretation of the results of the PCDD/F concentrations and the PMF analysis outlined above. Currently, we are in the process of determining whether there are additional indicators of products of dechlorination within the congeners provided in our results.

Developing an environmentally friendly water reuse technology using ferrate (VI)

Basic Information

Title:	Developing an environmentally friendly water reuse technology using ferrate (VI)
Project Number:	2013NJ338B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-010
Research Category:	Water Quality
Focus Category:	Treatment, Water Quantity, Acid Deposition
Descriptors:	
Principal Investigators:	Nanzhu Li, Yang Deng

Publications

1. Li, Nanzh., Yang Deng and Dibyendu. Sarkar (2013) Ferrate (VI) as a New Treatment Chemical for Water Reclamation , The 5th International Conference on Medical Geology, Arlington, VA, Paper No. 29-7
2. Li, N. and Y. Deng (2014) A New Ferrate (VI)-Based Water Reuse Technology , The American Water Works Association (AWWA) 2014 Annual Conference & Exposition, Boston, Massachusetts, June 2014 (In progress)
3. Li, Nanzhu and Yang Deng (2013) Ferrate as a New Treatment Chemical for Removal of Contaminants from Secondary Effluent , The 50th Association of Environmental Engineering & Science Professors (AEESP) Anniversary Conference, Golden, Colorado, July 2013 (Poster Presentation)
4. Li, Nanzhu Yang Deng (2013) The Performance of Removing Traditional Contaminants from Secondary Effluent Using Ferrate(VI) , The Hudson-Delaware Chapter of the Society of Environmental Toxicology and Chemistry (HDC-SETAC) 2013 Annual Spring Meeting, Edison, New Jersey, May 2013 (Poster Presentation)
5. A manuscript to Water Research is in preparation

(3) **Project Summary**:

Problem

With the dramatic increase in the world's population and water demand over the past decades, our development has been significantly restricted by water resources as a result of the limited water quantity and/or water quality degradation. Water reuse has been regarded as one of the most important ways to increase the availability of limited freshwater and to solve water crisis in the future. United States Environmental Protection Agency (USEPA) and New Jersey Department of Environmental Protection (NJDEP) have issued guidance to highly encourage water reclamation in the U.S. and the State of New Jersey, respectively (USEPA, 2004; NJDEP, 2005). However, currently available water reclamation technologies are limited by different reasons such as high costs (e.g. for membrane process), unreliable treatability, or complex and labor-intensive operation. As a result, there is an urgent need to develop new, effective, low-cost, and sustainable water reuse technologies.

A major and stable source of reclaimed water is the secondary effluent from municipal wastewater treatment plants (WWTPs). Currently, WWTP typically utilizes aerobic biological treatment (e.g. activated sludge process), with the purpose of removing biodegradable organic matters and suspended solids in municipal wastewater. However, a variety of pollutants are still present in secondary effluent, and need to be effectively removed, such as effluent organic matter (EfOM), nutrients, pathogens, and persistent micro-pollutants (e.g. estrogens). Among these pollutants, EfOM, a combination of natural organic matters (NOM), soluble microbial products (SMPs) and traceable harmful chemicals, is the major holdback why secondary treated wastewater is not widely reused (Shon et al., 2006). Another emerging concern is persistent micro-pollutants such as pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs).

Ferrate (VI) is an emerging oxidant with a higher redox potential (2.20V) than ozone (2.08V) (Jiang, 2007b; Sharma, 2010; Ghernaout and Naceur, 2011). It is considered an environmentally friendly oxidant due to its powerful oxidative capacity and nontoxic final products - ferric iron (Sharma, 2002; Ghernaout et al., 2011). Ferrate (VI) can function as an oxidant, coagulant, sorbent and disinfectant. Recently, ferrate (VI) has been verified to effectively treat drinking water, industrial/municipal wastewater, and ballast water. However, there is not any study on ferrate oxidation for water reuse. Previous efforts have individually demonstrated that ferrate can significantly remove a broad spectrum of water pollutants, such as chemical oxygen demand (COD) (Farooq and Bari, 1986; Jiang and Lloyd, 2002; Jiang et al. 2007a), total nitrogen (TN) (Carr and Erickson, 1988; Johnson et al., 1998; Sharma, 2010), total phosphorus (TP) (Lee et al., 2009), turbidity (Jiang and Lloyd, 2002; Cekerevac et al., 2010), organic matters, pathogens (e.g. total coliform and *E.coli*) (Jiang et al. 2006; Jiang et al., 2007a; Bandala et al., 2009), and emerging micro-pollutants such as pharmaceuticals (Jiang et al.2005; Lee and Gunten, 2005; Sharma, 2010). These unique treatment characteristics, plus its decreasing cost (~ $2/lb), allow ferrate (VI) to be a new and potential treatment chemical to achieve water reclamation in a single step. In this proposal, we evaluated the performance of ferrate (VI) oxidation for concurrent removal of multiple pollutants in secondary effluent, and examined whether ferrate(VI) can be used as a viable tertiary treatment for the purpose of water reuse.

Research Objectives

The **long-term goal** is to develop new, environmentally friendly and sustainable treatment technologies for water reuse. The primary **purpose** of this proposed project is to evaluate the technical and economic feasibility of ferrate as an emerging green agent for simultaneous removal of various pollutants from secondary effluent to achieve water reclamation. The **central hypothesis** is that different contaminants in secondary effluents can be significantly removed by ferrate (VI) through oxidation, coagulation, adsorption and disinfection. To test the hypothesis, we will answer the three following questions:

- What are the treatment efficiencies of ferrate (VI) for traditional contaminants in secondary effluent (i.e. COD, TN, TP, total coliform and *E. coli*)?
- What are the treatment capacity, kinetics pattern, and mechanism (oxidation vs. adsorption) of ferrate (VI) for removal of a representative emerging pollutant (estriol, E3)?
- What are the difference between ferrate (VI) treatment and the major water reuse technologies currently available in water reuse?

Methodology

Secondary effluent samples were collected from the secondary clarifier of Joint Meeting of Essex & Union Counties in Elizabeth, New Jersey. Samples were transported in amber glass jars and stored in a refrigerator at 4 ˚C until use. Water analyses were completed within a week.

Bench scale jar tests were conducted to evaluate the feasibility of Fe(VI) for treatment of the secondary effluent. Basic water quality parameters of the secondary are shown in **Table 1**. Here, the dimensionless oxidant dose (DOD) is used as Fe(VI) dose, defined as below.

$$DOD = \frac{Equivalent\ of\ Fe(VI) added}{Equivalent\ of\ COD_0} \qquad (1)$$

Where, COD_0 is the initial COD in untreated secondary effluent. Equivalents of Fe(VI) and COD_0 can be computed as follows.

$$Equivalent\ of\ Fe(VI) added = \frac{Fe(VI)}{18.6} \qquad (2)$$

$$Equivalent\ of\ COD_0 = \frac{COD_0}{8} \qquad (3)$$

Where, 18.6 and 8.00 are the equivalent weights of Fe(VI) and COD, respectively. Tests were carried out at two different initial pH (5.0 and 9.0) and Fe (VI) doses (DOD = 0.10-3.00). In a typical run, the Fe(VI) oxidation was completed under a rapid mixing (150 rpm), followed by a 30-min flocculation with a slow mixing (30 rpm). After the iron floc settled, the supernatant was collected for analysis. The parameters of untreated secondary effluent and supernatant were analyzed, including COD, DOC, UV_{254}, TP, nitrate nitrogen, ammonia nitrogen, total coliform and *E.coli*, as well as one target emerging contaminant (i.e. E3).

Table 1. Basic Parameters of Secondary Effluent from a Typical Secondary Wastewater Treatment Plant

Parameters	**Values**
pH	7.31-7.61
COD (mg/L)	32.9-38.7
TOC (mg/L)	43.5-57.7
UV_{254} (mg/L)	0.14-0.22
TP (mg/L)	4.00-5.76
NO_3-N (mg/L)	0.3-9.3
NH_3-N (mg/L)	15.2-20.2
E3 (ppb)	N/A
Total coliform (MPN)	~ 2.4×10^5
E. coli (MPN)	~ 410

Results and findings

(1) Fe(VI) performance for treatment of secondary effluent

The maximum removal efficiencies of different contaminants achieved by Fe(VI) are shown in **Figure 1**. As seen, all of the contaminants could be significantly removed under certain conditions. Results showed that Fe(VI) without pH adjustment could remove COD, DOC, UV_{254}, TP, nitrate nitrogen, ammonia nitrogen, E3 and OTC by 41%, 82%, 67%, 96%, 98%, 57%, 99% and 99%, respectively. Moreover, more than 99% total coliform and *E. Coli.* could be inactivated within 5 minutes. An acidic environment favored the ferrate treatment. For example, at pH 5.5, up to 59% COD, 78% UV_{254}, and 99% TP were removed, respectively. However, more ammonia nitrogen was removed under a basic condition, probably because ammonia molecules were more readily stripped at higher pH **(Figure 2)**. The disinfection effect of ferrate (VI) is shown in **Figure 3**. Very poor disinfection capacity was observed at an acidic condition (5~6), while, ferrate at pH 8-10 exhibited high inactivation ability. This finding is because different CT values (the product of the disinfectant dose and contact time with water being disinfected) was accomplished at different pH conditions. In a weakly acidic solution, the major Fe(VI) species was $HFeO_4^-$ that decays much more rapidly than FeO_4^{2-} that is the primary Fe(VI) species at pH 8-10. As a result, high CT was achieved at a weakly alkaline condition than at an acidic environment. Additionally, the high removal of UV_{254} indicates that ferrate preferentially attacked these organic molecules with aromatic rings. However organics mineralization expressed as the reduction of DOC was a little more difficult, suggesting that ferrate(VI) was a potential option for complete oxidation of organic wastes.

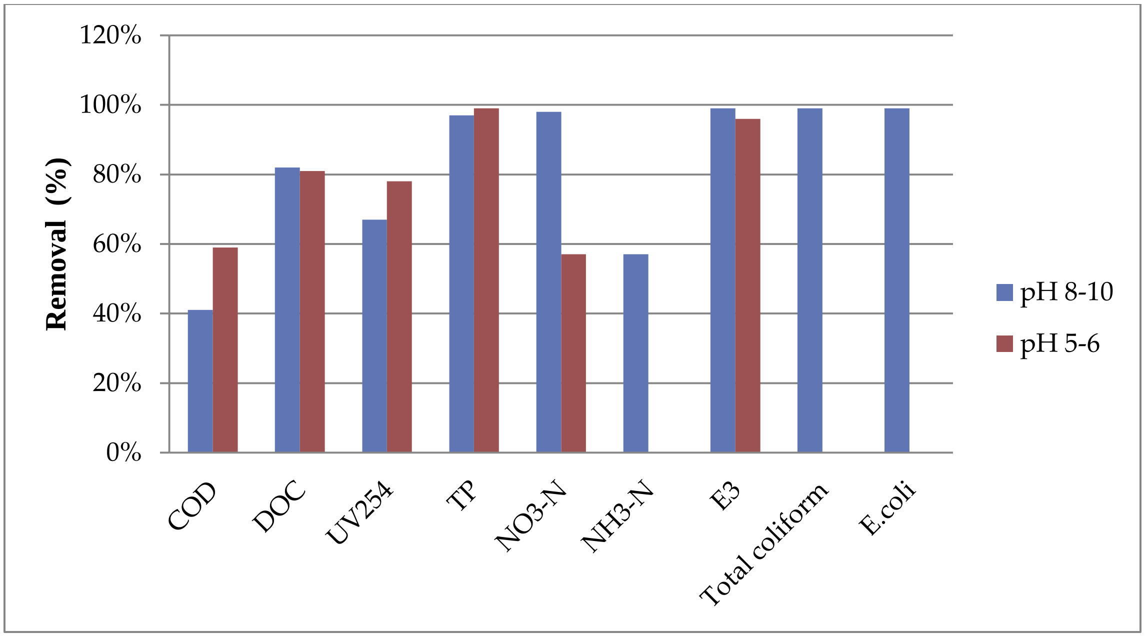

Fig.1 The maximum removal efficiencies of different contaminants achieved during Fe(VI) treatment of secondary effluent at different pH

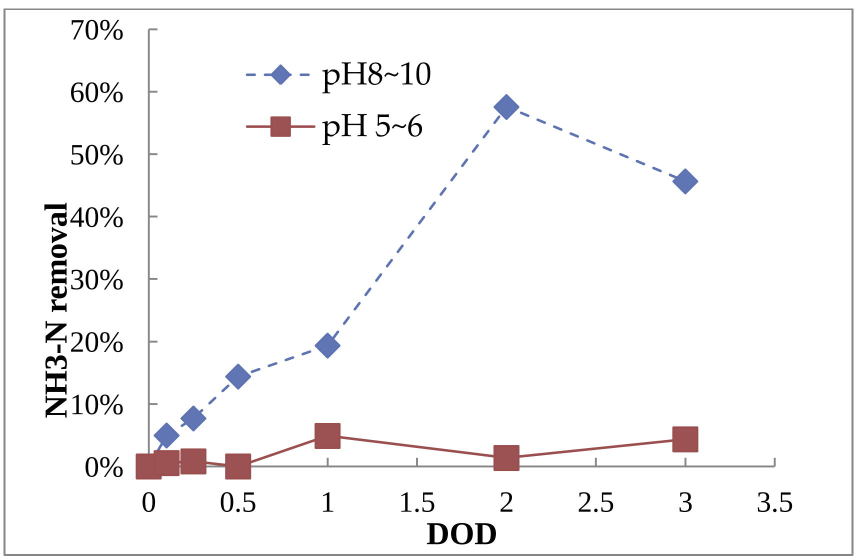

Fig.2 Ammonia nitrogen removal under different DOD and pH

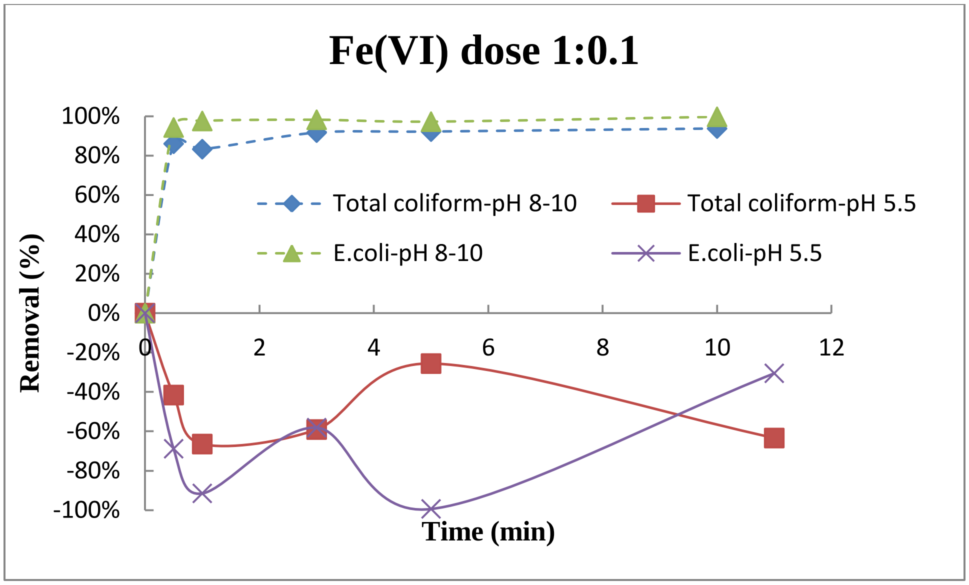

Fig. 3 The total coliform and *E.coli*. removal under different pH

(2) Oxidation *vs*. sorption

The produced iron hydroxide sludge was collected and recycled for treatment of secondary effluent at an iron sludge dose of 100-2000 mg/L. At the maximum, 42% COD and 94% TP were removed via adsorption **(Figure 4** and **5)**, but little DOC in the secondary effluent was reduced (data is not shown here). These encouraging results demonstrate that the produced iron sludge, the undesirable byproducts required for appropriate disposal, may be a pre-treatment prior to Fe(VI) treatment. Recycling sludge may significantly reduce the Fe(VI) dose in the following treatment, thereby having a potential to lower the treatment cost. Further studies are required to understand chemical structures and treatment patterns of the recycled sludge.

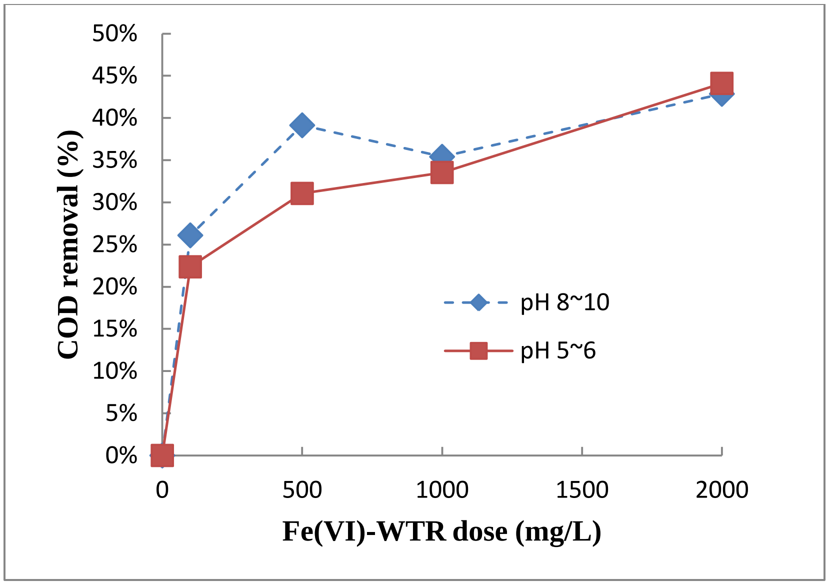

Fig.4 COD removal by Fe(VI) sludge

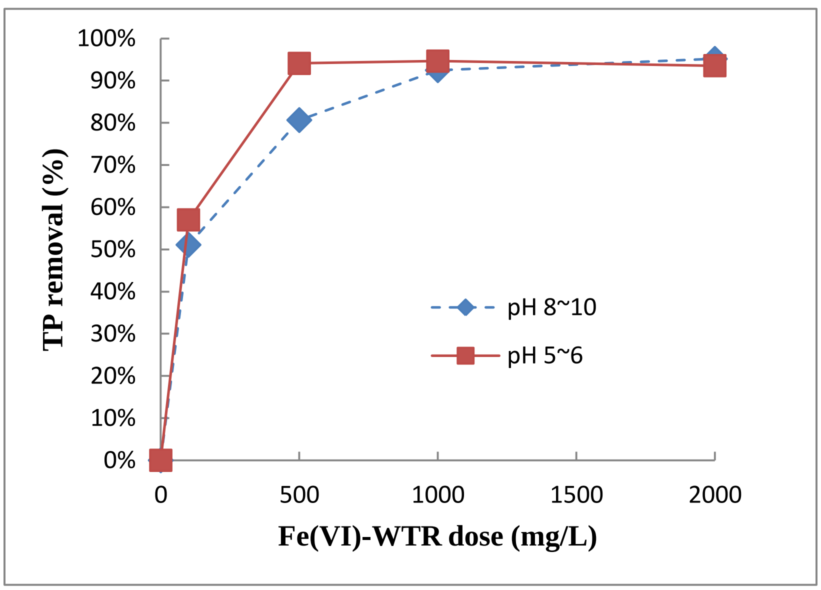

Fig. 5 TP removal by Fe(VI) sludge

Understanding the fate of MTBE in anaerobic aquatic environments of New Jersey

Basic Information

Title:	Understanding the fate of MTBE in anaerobic aquatic environments of New Jersey
Project Number:	2013NJ339B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-006
Research Category:	Water Quality
Focus Category:	Groundwater, Toxic Substances, Water Supply
Descriptors:	
Principal Investigators:	Tong Liu, Max M Haggblom

Publications

1. Liu Tong, Lora. R. McGuinness, Laura. K. G. Youngster, Lee. J. Kerkhof and Max. M. Häggblom, July 2013, Microbial Community Analysis of Anaerobic Methyl tert-butyl ether (MTBE)-degrading Enrichment Cultures, Gordon Conference of Applied & Environmental Microbiology, South Hadley, MA
2. Liu Tong, Hyeri Ann, Lora R. McGuinness, Lee J. Kerkhof and Max. M. Häggblom, May 2014, Comparing anaerobic MTBE-degrading communities from New Jersey and New York sediments, 99th NJWEA Annual Conference, Atlantic City, NJ

(4) Project Summary:

Groundwater contamination is a major problem in industrialized areas all over the world, and New Jersey is by no means an exception to this rule. Methyl tert-butyl ether (MTBE) is a particularly prominent contaminant in northeast of the United Sates. Between 2002 and 2008, it was detected in over 20% of New Jersey's public community and non-transient non-community water supplies. MTBE is a gasoline additive which improves the performance of engines while reducing hazardous combustion emissions. Unfortunately, even a small amount of MTBE dissolved in drinking water can cause a strong unpleasant odor and taste. More importantly, laboratory tests suggest that MTBE may also increase the risk of cancer. To this date, twenty-five states have signed legislation banning MTBE and more efforts are underway to reduce the concentration of MTBE in our groundwater supplies.

Among different natural approaches, biodegradation is a feasible method to reduce MTBE concentration in our groundwater. While biodegradation is efficient and inexpensive, it is challenging to monitor its progress *in situ*. An efficient assessment of *in situ* remediation and the precise identification of the microorganisms responsible for pollutant degradation are therefore important aspects of a successful implementation of biodegradation. Although it has been demonstrated that MTBE can be degraded naturally, the precise organisms and mechanism that are responsible are still unknown. The **aim** of my research is to develop tools for monitoring natural attenuation and to identify the organisms that are responsible for MTBE biodegradation in the groundwater of New Jersey.

(5) Methodology

In this study, enrichment cultures were selected for SIP experiments spiked with 13C labeled O-methyl carbon MTBE or 12C-MTBE. After 50% of degradation occurred, each 12C-MTBE culture was withdrew and respiked with either 12C acetic acid or 13C acetic acid (two carbon labeled). For each sample, DNA was extracted followed by CsCl gradient separation and amplification with universal bacterial primer (27F-1100R). The amplified DNA was digested with MnlI restriction enzyme and generated a fingerprint of each community by TRFLP analysis to determine the effects of cultural conditions on the communities.

(6) Principal Findings and Significance

So far I have successfully enriched several cultures which utilize MTBE as their sole carbon source. All the cultures are maintained under stable conditions such that the reduction of the MTBE concentration can be monitored over time. The cultures are now highly enriched with organisms that are closely linked to the MTBE-degradation process. In order to identify and characterize active bacteria, I have applied various genetic techniques such as Terminal Restriction Fragment Length Polymorphism (T-RFLP) analysis, Stable Isotope Probing (SIP) and clone library analysis. The TRFLP- SIP analysis has demonstrated that the organisms responsible for degrading MTBE belong to a small set of phylotypes of *Firmicutes*, *Synergistetes*, and *Deltaproteobacteria*.

My ultimate goal is to establish a direct connection between the MTBE degraders and their ecological function in the natural environment. This will enable us to employ these organisms as “biomarkers” for *in situ* biodegradation. It is therefore essential to pinpoint as precisely as possible which specific organisms are responsible for the degradation. This requires specialized techniques that are capable of tracking individual cells, such as single-cell resonance Raman (SCRR) microspectroscopy. Since these facilities are not present in New Jersey, I plan to make use the infrastructure and expertise of the laboratory of Dr. W. Huang in Sheffield University (UK). To optimize our chances for success, I will visit their lab in person to carry out the experiments in collaboration with the local experts in September.

Effect of cadmium on accelerated metamorphosis induced by hormesis in larvae of Chironomus riparius (Diptera:Chironomidae)

Basic Information

Title:	Effect of cadmium on accelerated metamorphosis induced by hormesis in larvae of Chironomus riparius (Diptera:Chironomidae)
Project Number:	2013NJ340B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-010
Research Category:	Biological Sciences
Focus Category:	Ecology, Toxic Substances, Water Quality
Descriptors:	
Principal Investigators:	Jun T Oh, Carolyn Summerill Bentivegna

Publications

1. Publication (accepted 3/26/2014) Oh, Jun. T; Epler, John. H; Bentivegna, Carolyn. S, 2014, A Rapid Method of Species Identification of Wild Chironomids (Diptera: Chironomidae) via Electrophoresis of Hemoglobin Proteins in Sodium Dodecyl Sulfate Polyacrylamide Gel (SDS-PAGE), Bulletin of Entomological Research.
2. Oh, Jun. T; Bentivegna, Carolyn. S, 2013, The effect of cadmium on ubiquitin-proteasome pathway (UPS) involved in degradation of hemoglobin proteins in larvae of 4th instar Chironomus riparius (Diptera: Chironomidae), in Hudson-Delaware Regional Chapter of the Society of Environmental Toxicology and Chemistry, Jamaica Bay Wildlife Refuge, NY.
3. Oh, Jun. T; Bentivegna, Carolyn. S, 2013, The effect of cadmium on ubiquitin-proteasome pathway (UPS) involved in degradation of hemoglobin proteins in larvae of 4th instar Chironomus riparius (Diptera: Chironomidae), in Society of Environmental Toxicology and Chemistry North America 34th Annual Meeting, Nashville, TN pg 24.
4. Oh, Jun. T; Bentivegna, Carolyn. S, 2014, The effect of cadmium on ubiquitin-proteasome pathway (UPS) involved in degradation of hemoglobin proteins in larvae of 4th instar Chironomus riparius (Diptera: Chironomidae), in The Petersheim Academic Exposition 2014, Seton Hall University, South Orange, NJ .

Project Summary

Problem:

Our laboratory's focus has been developing a biomarker that can be used to assess the aquatic environment. Our long term goal is to characterize various molecular responses that are exhibited by organisms upon a change in their environment – especially upon exposure to heavy metals. Heavy metals are frequent toxic pollutants in urban regions of New Jersey. For example, Kearny Marsh, located in the New Jersey Meadowlands between the Passaic River and Hackensack Rivers, is surrounded by major highways and highly urbanized areas. The water quality of Kearny Marsh was found to have supersaturated dissolved oxygen, high pH, and low oxidation-reduction potential, which are all indicative of eutrophication (Oh 2009). More importantly, there were at least 10 times higher levels of cadmium (Cd) and lead (Pb) in the sediment collected from Kearny Marsh when compared to that of the sites otherwise well preserved and located at a great distance from urbanized areas (Oh 2009).

Among many freshwater benthic macroinvertebrates, chironomids are one of the most ubiquitous, abundant, and ecologically diverse organisms (Timmermans *et al.* 1992 & Voshell 2002). Chironomids are one of the dominant species found at Kearny Marsh as well as other bodies of water in New Jersey and are therefore a good animal model for studying environmental quality in our state. Chironomids are somewhat different from other macrioinvertebrates in that chironomids have high concentrations of hemoglobin (Hb) proteins. The abundance and presence of Hb in chironomids is physiologically relevant as they allow the larvae to sustain aerobic metabolism under adverse environmental conditions such as polluted and hypoxic sediments (Lee *et al.* 2006). Chironomids are holometabolous insects and pass through four distinct stages in their life cycle (Chetelat *et al.* 2008) Interestingly, as the larva develops through four successive instars, various Hb proteins begin to appear gradually increasing as larvae reach later instars (Bergtrom *et al.* 1976 & Schin *et al.* 1974) This change in the relative concentration of Hb proteins during development has suggested activation and inactivation of gene loci at specific stages of development (Schin *et al.* 1974). Specific molecular mechanisms that explain the synthesis and degradation of Hb proteins during chironomid development are still unknown. Understanding the mechanisms associated with normal Hb regulation and any effects of heavy metals on them is essential for developing Hb as a biomarker of environmental stress in chironomid.

Previous literature supports the notion that environmental contamination can influence chironomids at both the molecular and cellular level, including expression of certain genes associated with various toxicological responses that impact individual fitness (Lee *et al.* 2006 & Timmermans *et al.* 1992). It is also well documented in the scientific literature that organisms exposed to pollutants have demonstrated hormesis – an event where a disruption of homeostasis yields a compensatory mechanism that is characterized as a low dose stimulation and high dose inhibition (Nascarella *et al.* 2003). In our previous acute cadmium (Cd) toxicity test, we observed that at 0.3 µM of Cd there was an increase in production of digested Hb proteins – meaning that either the synthesis of Hb proteins could have been up-regulated yielding higher concentrations of Hb proteins to be digested and/or the rate of digestion of the Hb proteins could have been accelerated. In some cases, earlier and higher pupation was seen when compared to the control group. However, in the higher concentration of Cd, there was a loss of Hb proteins, suggesting that Cd could inhibit the synthesis of Hb proteins or induce adverse effects on chironomid resulting in an abnormal physiological response.

One of the ways that environmentally relevant concentrations of Cd could induce hormetic responses in chironomid is by altering the rate of metamorphosis. Abnormal metamorphosis could be due to increased expression of ecdysone and its receptor (EcR), which is thought to be abnormally up-regulated by high levels of degraded Hb protein and/or over expression of ubiquitin (Ub), a regulatory protein which marks damaged proteins for degradation by proteasome. The proposed idea is that enhanced degradation of Hb proteins could be caused by Cd binding to Hb proteins and/or their heme groups and triggering of Ub gene over expression. Our previous findings suggest that the increased intensity of low MW Hb bands on sodium dodecyl sulfate polyacrylamide gel (SDS-PAGE) at low Cd exposure could be explained by enhanced Hb degradation by Ub, while decreases in both high and low MW Hb bands at high Cd exposures is explained as Cd interference with multiple cellular targets effecting transcription and translation rates globally (Figure 1). Therefore, in this study, expression of EcR, Ub, and Hb IV/VII genes was investigated in *Chironomus riparius* larvae. We examined how low concentrations of Cd might trigger hormetic responses and also measured physiological and molecular processes involved in chironomid during its 4th instar, pupa and adult fly stages.

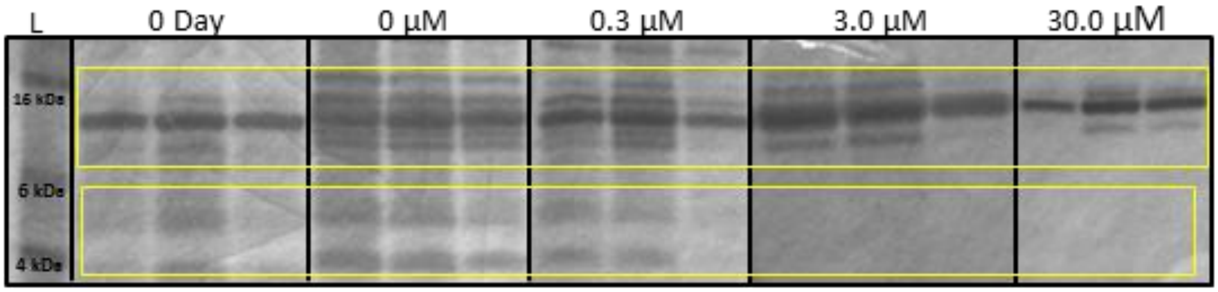

Figure 1. Hemoglobin band patterns of individuals that participated in 96 h Cd acute toxicity tests. Each lane represents the Hb protein profile of one larva. On the left, a molecular ladder showing the sizes of the bands. The affected regions are approximately from ~ 4 to 16 kDa. Increased time and concentration (µM) of Cd resulted in decreased levels of both low and high MW proteins as indicated by the yellow box. 0 day individuals were from the culture tank at the start of the experiment. 3 individuals from each group is shown.

Specific objectives and hypotheses

The specific objectives of the proposed research as follow:

1. Examine the physiological effects of different Cd concentrations on chironomid including growth, survival, and rate of emergence during its life cycle
2. Characterize gene expression of Hb IV and VII to determine whether either is up- or down-regulated during Cd exposure
3. Identify, clone, and sequence mRNAs of EcR and Ub and determine if they are regulated by different concentrations of Cd
4. Compare changes in gene expression with changes in Hb protein profiles

The overall goal is to further define and develop Hb protein profiles as a bio-monitoring tool for water quality assessment. The proposed research is investigating molecular mechanisms that might alter Hb profiles shown on SDS-PAGE. The *specific hypothesis* is that abnormal Hb protein degradation due to low toxicant concentrations is associated with premature metamorphosis in chironomid, a phenomena associated with hormesis. Pre-mature metamorphosis will be associated with abnormal expression of EcR, Ub and Hb IV and VII genes.

Methodology

Laboratory cultured larvae of *C. riparius* were reared to second instar from the same fertilized egg masses. From the total population, 30 larvae were randomly picked and used for each concentration – 0, 0.1, 0.3, and 3.0 µM Cd (Sigma Chemical Co., St. Louis, MO). Acidwashed sand was provided as a substrate and larvae were fed daily. The test water was obtained by making reconstituted water (US EPA 2006) from the ½ deionized water (Millipore Milli-Q, Billerica, MA) and ½ filtered tap water with reagent grade chemicals: $NaHCO_3$, $CaSO_4$, $MgSO_2$, and KCl (Sigma). The average hardness of the reconstituted water was between 160 to 180 ppm, the average pH was between 7.2 to 7.4, the average temperature was between 20 to 21 °C, and the dissolved oxygen was between 7 to 9 ppm. The test water (250 ml) was added to 1 L polypropylene containers, and $CdCl_2$ was spiked into it from a stock concentration. Approximately 80% of the test water was aerated and changed every 24 hours, and a new spike was added. At the end of the study, the percent recovery of actual concentration of Cd in the water for 0.1 (not tested) 0.3 µM and 3.0 µM was, 86% and 52%, respectively (Molecular Probes, Eugene, OR) Acute tests lasted 96 hours and lifecycle tests were concluded at 25 days even if not all chironomids had pupated or emerged.

For lifecycle tests, effects of Cd on physiological responses were tracked by determining survival and pupation and emergence success. Pupation success rate was calculated by counting the number of pupa versus the total number of chironomids added to a vessel. Emergence success rate was calculated by counting the number of adults that emerged versus the total number of pupa in a vessel. More subtle effects on chironomid physiology were measured by determining the dry weight of both larvae and adult flies.

Both chironomid larvae and pupae were collected for characterizing expression of the following genes: EcR, Ub, and Hb IV/VII. Total RNAs were extracted by homogenizing three larvae or pupae in TRIzol (Invitrogen, Carlsbad, CA). From the total RNAs, a cDNA library was constructed using oligo-dT primers (Applied Biosystems, Foster City, CA). The cDNA was used as a template to amplify genes of interest with PCR. Primers for EcR, Hb IV/VII, and β-actin were generated based on the nucleotide sequences information available in National Center for Biotechnology Information (NCBI). The cDNA was used as a template for analyzing gene expressions of EcR, Hb IV, and Hb VII using quantitative polymerase chain reaction (qPCR). The ΔΔCt method was chosen to calculate relative gene expression, and all data were normalized against β-actin, as a housekeeping gene (Livak 2001).

The sequence for Ub was not available in NCBI, and it was necessary to first generate degenerative primer sets for Ub gene in order to develop gene specific primers for qPCR. Degenerative primers were generated based on the available sequence homology among five closely related species: *Aedes aegypti*, *Culex quinquefasciatus*, *Drosophila melanogaster*, and *Papilio xuthus*. Using degenerative primers, multiple bands of the anticipated size were observed on an agarose gel stained with ethidium bromide. Of those, three distinct bands (100, 400, and 600 base-pairs) were excised, cloned, and then sequenced at Genewiz, Inc. (South Plainfield, NJ).

Principal Findings and Significance

Objective 1: Examine the physiological effects of different Cd concentrations on chironomid including growth, survival, and rate of emergence during its life cycle

Concentration-response studies showed no significant difference between control and 0.1 and 0.3 µM Cd for survival. Larvae exposed to 3.0 µM Cd did not develop further into later instars. Their growth was arrested approximately at the beginning of 3rd instar, and the mortality rate was high. Those that survived remained much smaller in size than those exposed to lower concentrations of Cd. Therefore, chironomids in 3.0 µM Cd were seized after 10 days and collected for RNA analysis. This particular observation was significant in that it results were similar to the study by Williams *et al.* 1986 where it was observed that the early stages of larva (2nd instar) showed approximately 8 fold higher sensitivity (24 hour LC50) towards cadmium than that of the 4th instar.

Pupation and emergence success rates were monitored for 25 d since each rate illustrates the toxicity of Cd to the chironomid's whole life cycle. Figure 2 shows data on the success rates of pupation, metamorphosis from 4th instar to pupa. Both 0.1 and 0.3 µM chironomids showed a significant reduction in pupation rates. At 0.1 and 0.3 µM Cd, Cd was shown to inhibit metamorphosis by reducing pupation rate by more than 50% when compared to that of the control. It appears that since chironomids were exposed to Cd during early stages, even at low concentrations, Cd somehow interfered with larval development. However, it was observed that once larva made the transition into pupa, emergence into the adult fly was successful regardless of Cd concentration (data not shown). Although both pupation and emergence success rates require further examination for an accurate assessment, at this time, pupation appears to be the most sensitive event in the chironomid's life cycle. Williams *et al* (1986) suggested that pupae show more resistant to Cd than fourth instar larvae, indicating that pharate, which is the exoskeleton of pupa, could be reducing Cd availability. Therefore, once a larva makes the transition into the pupa stage, it is likely to emerge into an adult fly.

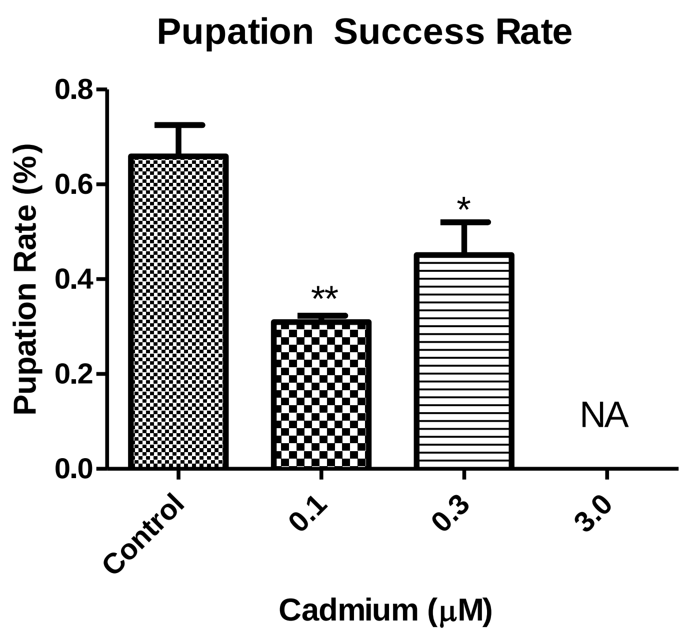

Figure 2. Pupation success rates for each concentration of Cd. Pupation rate was calculated by counting the number of pupa divided by the total number of chironomids. The number of pupae counted for each concentration of Cd: n=29 (Control), n= 14 (0.1 μM), and n=9 (0.3 μM). The values with * indicate significant difference when compared to the control ($p<0.005$). The data were analyzed using one-way ANOVA with Dunnett's Multiple Comparison Test to the control.

In order to understand the mechanism of action on how Cd affects the pupation and emergence rates, it was necessary to measure growth. Growth and pupation/emergence are closely related such that environmental factors that affect larval development may also affect emergence success. Previous studies have shown that there appears to be a link between larval growth – a threshold weight – and how it could negatively influence emergence rate if the weight of larva falls below the threshold (Liber *et al*, 1996, Sibley *et al*, 1997). Figure 3 shows the average tissue mass (dry weight) of larvae exposed to each concentration of Cd. Both control and 0.1 μM Cd treated larvae appeared to be within the optimal range, as suggested by Sibely *et al* where there is a minimum tissue mass threshold of approximately 0.6 mg dry weight for a larva to undergo metamorphosis into a pupa and for emergence of the adult to take place. Larvae exposed to 0.3 μM Cd, but which did not pupate by 25 days, showed a significant reduction in tissue mass, and this reduction in weight was congruent with the lower pupation success rate

(Figure 2). Interestingly, the tissue mass of adult flies from 0.3 µM Cd was observed to be no different than 0.1 µM Cd and control (Figure 4). This suggested that larvae which were able to pupate by 25 day had sufficient threshold weight to achieve normal adult size.

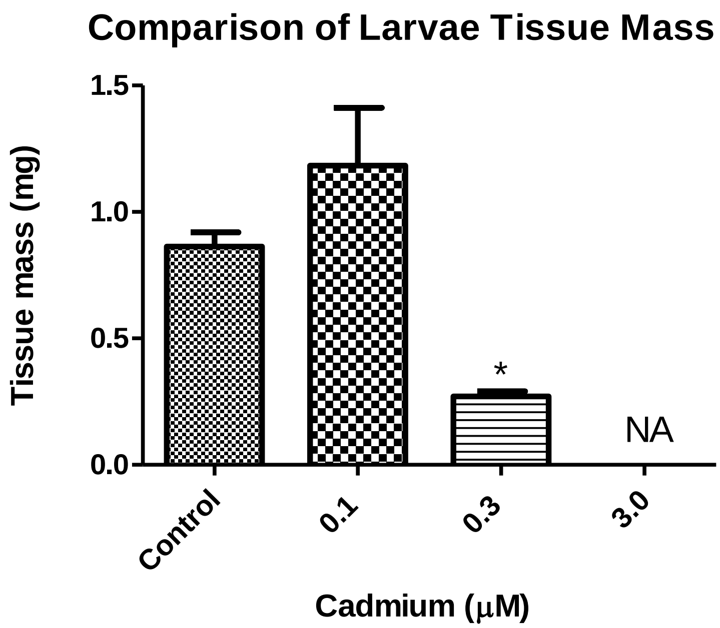

Figure 3. Comparison of dry-weight of larvae exposed to different Cd concentrations. Larvae were collected at 25 days and oven-dried for 24 hours. The dry weight per larva was measured in mg. Larvae exposed to 3.0 µM Cd did not develop beyond 2nd instar and were not weighed. The values with * indicate significant difference when compared to the control ($p<0.005$). The data were analyzed using one-way ANOVA with Dunnett's Multiple Comparison Test to the control.

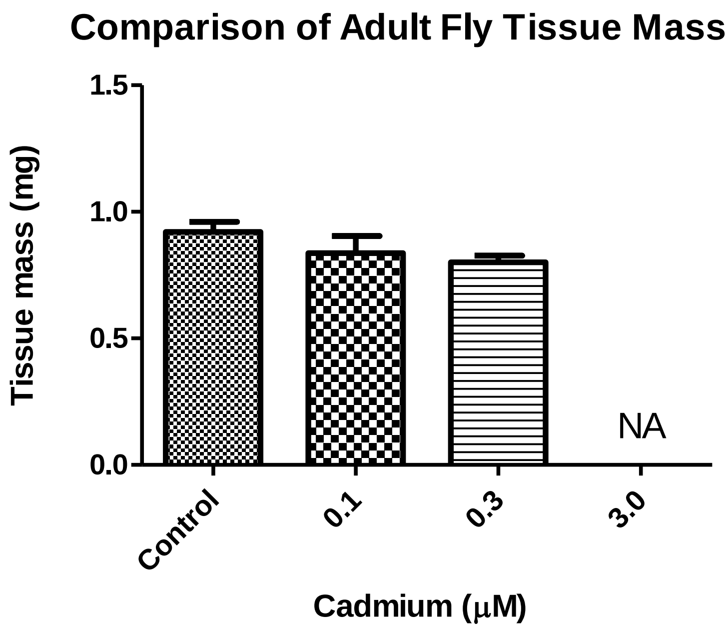

Figure 4. Comparison of dry-weight of adult flies emerged from pupae. Adult flies were collected and oven-dried for 24 hours. The dry weight per adult fly was measured in mg. Dry-weight for 3.0 μM is not available. The values with * indicate significant difference when compared to the control ($p<0.005$). The data were analyzed using one-way ANOVA with Dunnett's Multiple Comparison Test to the control.

Objective 2: Identify, clone, and sequence mRNAs of EcR and Ub and determine if they are regulated by different concentrations of Cd

Gene specific primers for Hb IV, Hb VII, and β-actin were previously generated and verified by our laboratory. However, primers for EcR and Ub had not been developed by the lab. The DNA sequence for chironomid EcR was available in NCBI that for Ub was not. Using information and tools from NCBI, primers were generated for EcR and Ub and verified by molecular cloning and sequencing. This resulted in gene specific primers for *C. riparius* that could be used in qPCR analyses.

The gene specific primers developed for EcR of *C. riparius* were able to bind to and amplify the expected target gene. Figure 5 shows 100% identity of the query, cloned and sequenced PCR product, and the subject, nucleotide sequence available in NCBI (accession number: KJ135024). This information has confirmed that the sequence acquired from molecular cloning followed by sequencing was in fact EcR gene. The primer set for EcR forward primer was 5'**GACCTGGCATAGTTGGAAGTAA**3' and for reverse primer was 5'**GCGGTGGATCACATTTCATAAG**3'. With this particular primer set, a 138 base-pair partial region of EcR was amplified (data not shown) and used for qPCR.

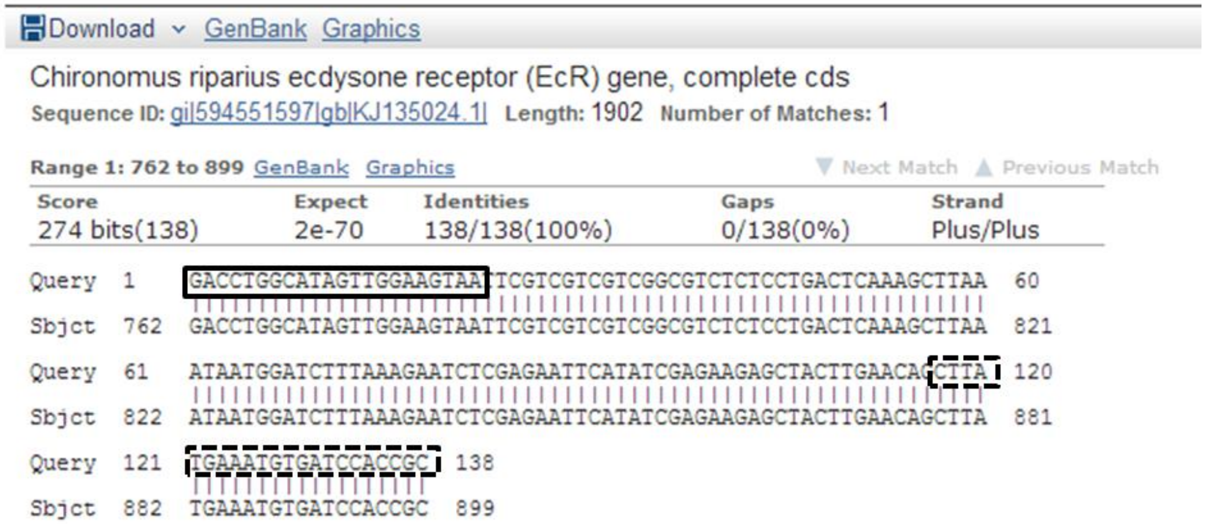

Figure 5. Cloned and sequenced nucleotide information of ecdysone receptor gene (EcR). An 138 base pair (bp) query sequence (cloned) was matched up with the subject sequence (annotated genomic nucleotide sequence available in NCBI, accession number: KJ135024) with 100% identity confirming EcR of *C. riparius*. A gene specific primer set containing forward primer (indicated by the black box) and reverse primer (indicated by the dotted box) was generated to in order to amplify this partial region of the gene.

Gene specific primers for Ub involved starting with alignment of NCBI available sequences of other species. From the alignment, degenerative primers based on the consensus sequence were found. Standard PCR amplification with these degenerative primer sets provided several potential gene products detected as bands on ethidium bromide stained agarose gels. The most intense band was excised and the DNA from that band was purified as a template for molecular cloning. The sequence information from that particular band is shown in Figure 6 as the query sequence. Since there was no genomic nucleotide sequence information available for chironomid Ub, one of the most closely related species, *Aedes aegypti*, was chosen as a subject match. The alignment showed 86% identity confirming that the cloned band was a partial sequence of Ub. From the initially acquired sequence, a gene specific primer set was generated containing a forward primer of 5’**ATCAGACAATGTACGACCATCTT**3’and a reverse primer of 5’**ACATAGGAAGTTGAGCCATCAG**3’. This primer set amplified a 135 base-pair partial region of Ub in *C. riparius*.

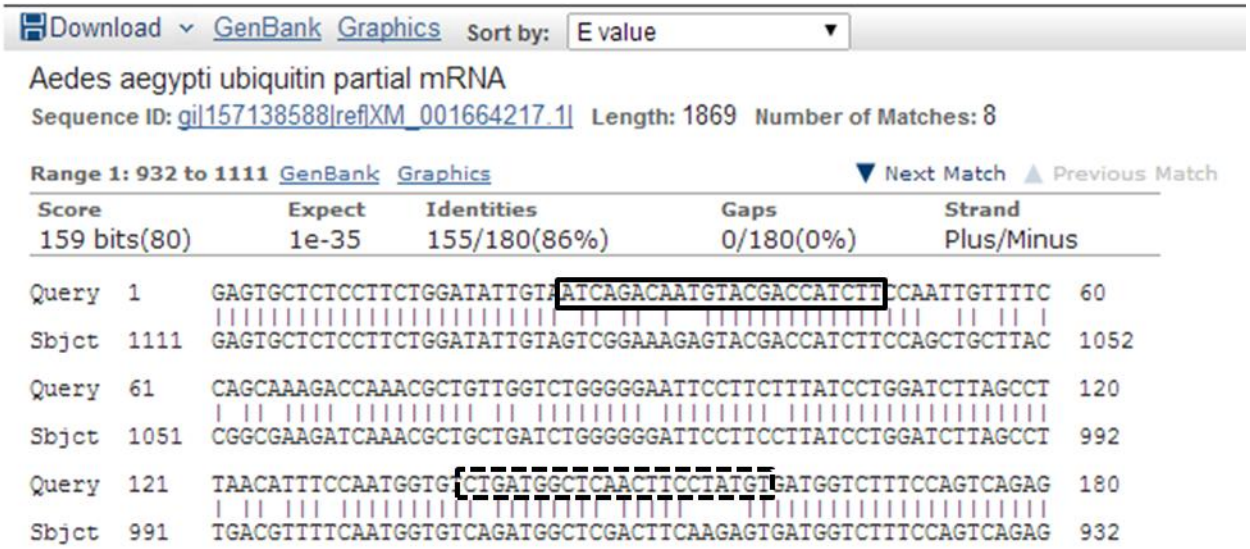

Figure 6. Cloned and sequenced nucleotide information of ubiquitin (Ub) gene. Since ubiquitin gene of *C. riparius* is currently unavailable, the query sequence (cloned) was matched up with the subject sequence of one of the closely related species, *Aedes aegypti* (annotated gene sequence available in NCBI, accession number: XM_001664217) with 86% identity, confirming ubiquitin gene of *C. riparius*. Primer set containing forward primer 5'ATCAGACAATGTACGACCATCTT3' (indicated by the black box) and reverse primer 5'ACATAGGAAGTTGAGCCATCAG3' (indicated by the dotted box) was generated in order to amplify a partial region (135 base-pairs) of Ub using qPCR.

Prior to moving onto qPCR gene expression analysis, the Ub primer set tested in PCR. The PCR result showed multiple nonspecific bands of various sizes (Figure 7). Although a 135 base-pair band was generated, at least four distinct nonspecific bands were also produced from the gene specific primer set. qPCR requires that there be one specific gene fragment generated, so more work is needed before Ub expression can be determined.

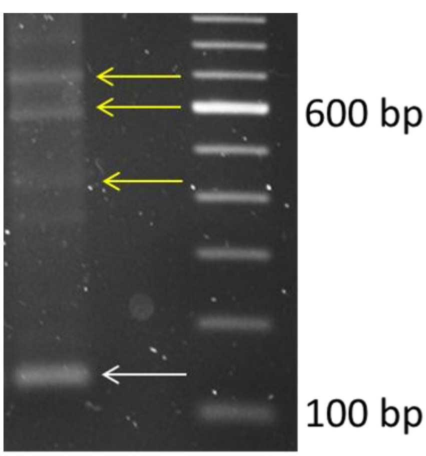

Figure 7. Agarose gel showing amplified ubiquitin gene product. Purified genomic DNA was used as a template for PCR amplification with ubiquitin primer set. White arrow indicates the intended PCR product (138 base-pairs) and yellow arrows indicates nonspecific products. Molecular ladder is shown on the right.

Objective 3: Characterize gene expression of EcR, Hb IV and VII to determine whether either is up- or down-regulated during Cd exposure

Gene expression of EcR, Hb IV, and VII was analyzed using qPCR in order to determine whether Cd exposure could either up- or down-regulate the expression of those genes. Figure 8 shows the relative mRNA expression for EcR where there was no statistically different regulation of EcR upon Cd exposure. The relative mRNA expression values were compared to the control ($p<0.005$). Interestingly, individuals exposed at 0.1 µM Cd showed a slight down-regulation of EcR, which was unexpected and opposite of what was hypothesized. Overall, EcR was shown to be consistently expressed regardless of the concentration of Cd tested.

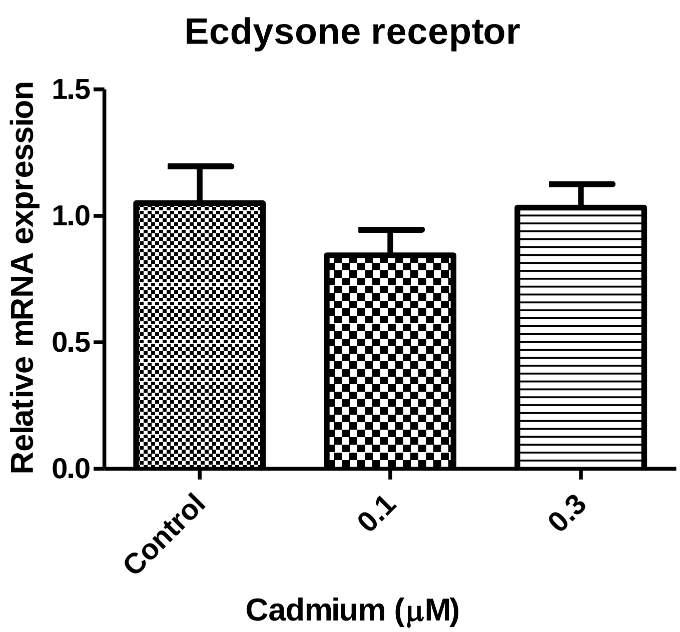

Figure 8. mRNA expression of ecdysone receptor (EcR) in C. riparius exposed to 0, 0.1 and 0.3 µM of Cd for 25 days. The values are expressed as relative mRNA expression. The values with * indicate significant difference when compared to the control ($p<0.005$). The data were analyzed using one-way ANOVA with Dunnett's Multiple Comparison Test to the control.

Figure 9 represents the relative mRNA expression for Hb IV gene. Hb IV gene showed a dose-response where there was a significant down-regulation of Hb IV in both 0.1 and 0.3 µM of Cd treatment groups, 23% and 87% reduction, respectively ($p<0.005$). This observation contradicted our hypothesis that Cd would bind to Hb proteins by replacing iron or oxygen molecules and thereby stimulate the synthesis of Hb proteins. However, Hb IV gene seemed to be highly sensitive towards Cd exposure even at 0.1 µM, which is less than what is considered to be an environmentally relevant concentration.

Unlike Hb IV, Hb VII was shown to be not affected by Cd exposure (Figure 10). Although there seems to be a slight increase in Hb VII expression in the Cd treated groups suggesting that Cd stimulated the expression of Hb VII genes, the values were not statistically different from control. Regardless, this observation indicated that Hb VII was continually expressed by larvae exposed to both concentrations of Cd.

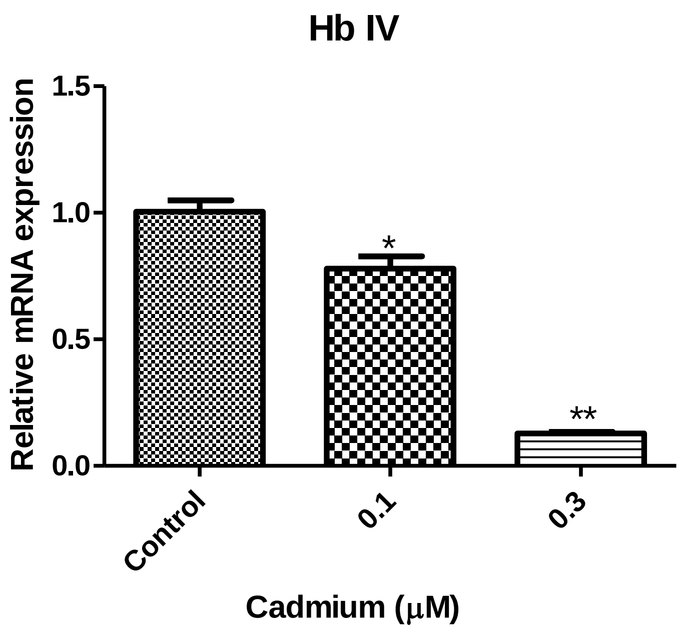

Figure 9. mRNA expression of Hb IV in *C. riparius* exposed to 0, 0.1 and 0.3 µM of Cd for 25 days. The values are expressed as relative mRNA expression. The values with * indicate significant difference when compared to the control ($p<0.005$). The data were analyzed using one-way ANOVA with Dunnett's Multiple Comparison Test to the control.

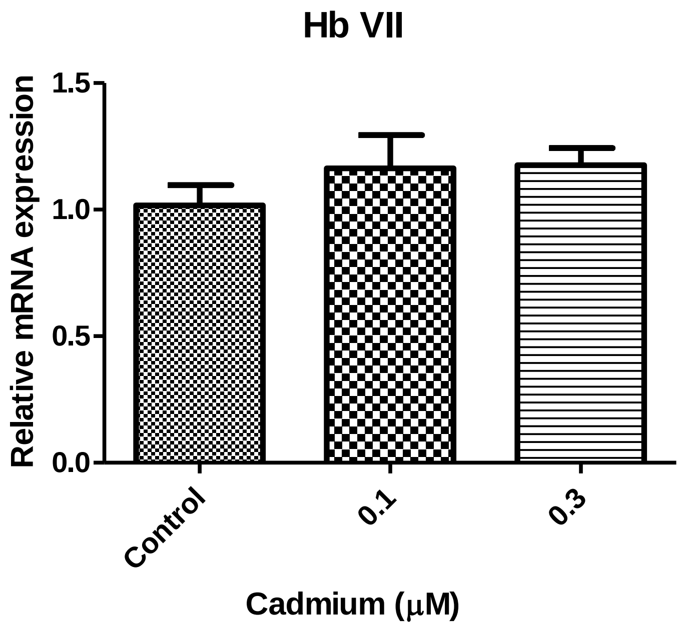

Figure 10. mRNA expression of HB VII in *C. riparius* exposed to 0, 0.1 and 0.3 μM of Cd for 25 days. The values are expressed as relative mRNA expression. The values with * indicate significant difference when compared to the control ($p<0.005$). The data were analyzed using one-way ANOVA with Dunnett's Multiple Comparison Test to the control.

Objective 4: Compare changes in gene expression with changes in Hb protein profiles

In order to understand the mechanisms by which synthesis of Hb protein is regulated, it was necessary to investigate Hb protein levels during chironomid development under control conditions. Figure 11 depicts changes in Hb protein profile in 2nd instar through adult fly of *C. riparius* as detected on PAGE gels. Under control conditions, a band at 12.5 kDa was initially synthesized in 2nd instar andwas continuously synthesized throughout the whole life cycle. The band at 12.5 kDa was analyzed and confirmed by liquid chromatography–mass spectrometry to contained predominantly Hb VII (data not shown). The abundance and presence of Hb VII was consistently high inacute Cd toxicity test even at the highest concentration tested, 30 μM (Figure 1). This corresponded with qPCR gene expression (Figure 10) where HB VII expression was not significantly affected by Cd exposure at the concentrations tested.

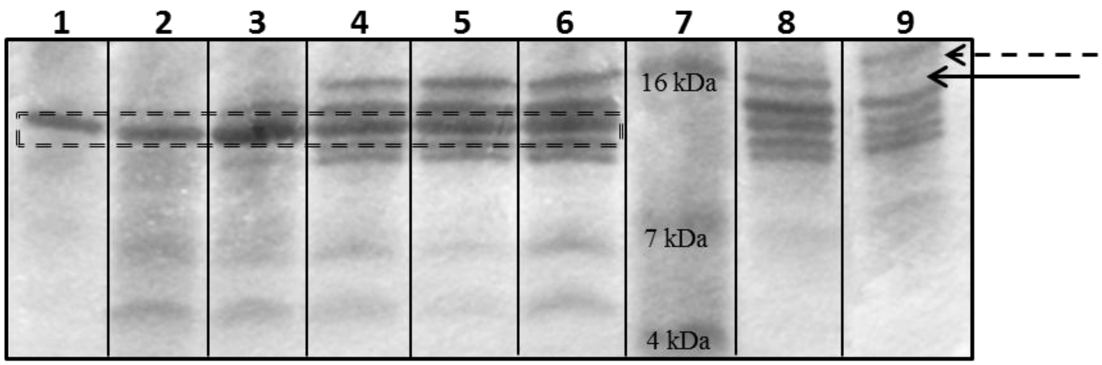

Figure. 11 Changes in Hb protein throughout the life cycle of a laboratory population of *C. riparius*. Dotted box indicates 12.5 kDa band. Each lane presents one of three samples collected at the same time point. Lane 1: 2nd instar, lane 2: 3rd instar, lanes 3, 4, 5, and 6: 4th instar, lane 7: ladder, lane 8: pupa, and lane 9: adult. Dotted black arrow indicates newly synthesized band. Black arrow indicates loss of the original 15.5 kDa band, which was present starting at fourth instar.

Chironomids showed sensitivity towards Cd treatments during development. Concentrations of 3.0 μM caused 80% mortality, concentrations of 0.1 and 0.3 μM significantly reduced pupation rate and concentrations of 0.3 μM reduced larval weight of unpupated larvae. It appeared that if pupation occurred emergence was successful, indicating that pupation might be a key stage in their life cycle. Successful emergence rate showed a close relationship with the larvae maintaining a threshold body mass, where it was observed that Cd exposed larvae showed a significant reduction in body mass, but those emerged to adult flies retained the threshold body mass. This finding indicated that a successful emergence was directly correlated with the threshold body mass required during larval stages. The Cd concentrations tested did not show the anticipated hormetic response on development, as mortality, growth and pupation rate were all negatively affected. Future studies will test lower concentrations.

This study showed that chironomids secrete different types and levels of Hb during development (Figure 11). qPCR gene expression analyses indicated that Hb IV expression was down regulated showing a concentration related response. Expression of EcR and Hb VII were not different from control, indicating that synthesis of Hb IV was inhibited by the Cd, potentially explaining the disappearance or loss of certain Hb bands in SDS-PAGE during acute toxicity tests (Figure 1). The consistent expression of Hb VII in life cycle tests (Figure 10) during Cd exposure could explain the presence of the 12.5 kDa in acute tests, even at 3.0 μM Cd. Interestingly, the expression of EcR did not change at that concentrations tested, which may be why no hormesis occurred. Further studies include optimization of the Ub gene primers and investigating the effects of Cd on Ub and Hb levels during the development so that regulation of Hb, especially Hb IV can be better understood.

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Assessing the role of wetland flora as a sink for nutrients in subsurface gravel wetlands in New Jersey

Basic Information

Title:	Assessing the role of wetland flora as a sink for nutrients in subsurface gravel wetlands in New Jersey
Project Number:	2013NJ341B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-004
Research Category:	Water Quality
Focus Category:	Nutrients, Non Point Pollution, Wetlands
Descriptors:	
Principal Investigators:	Kyle Seiverd, Louise Wootton

Publications

There are no publications.

(3) **Project Summary**:

Few of the studies to date on the role of plants in nutrient sequestration have been carried out in the field, and in my literature review I found few that were carried out in New Jersey. Thus it is imperative to assess the potential of various plant species commonly used in storm water basin plantings for removing nutrients from runoff in order to guide best management practices (BMP) in future basin designs. In addition, plant community composition is influenced by water level, amounts of leaf litter and soil fertility (Weiher and Keddy 1995). Thus, it might be expected that different plants will outcompete others in different wetlands. Determining which species are most successful in establishing in the different wetlands can help managers to select planting palettes that will be effective for the type of wetland in question.

The expected outcomes of this project will be to provide data on the short-term effects of stormwater basin design on the competitive outcomes between plant species, as well as on their biomasses, and nutrient content. In addition, we will provide data on seasonal changes in plant nutrient sequestration. Together, these data can be used to guide choices of plants for use in storm water basin plantings as well as to inform decision making about optimal harvest times for maximizing nutrient removals from systems such as these.

Methodology - give a general summary of procedures and methods actually implemented

Four subsurface gravel wetlands, each of a varying design will be constructed at Georgian Court University. Eight wetland plant species will be monitored during the growing season to assess establishment success and survival. These plants will also be analyzed for nutrient content at the beginning, mid and end of growing season. Nutrient analyses will be done at Rutgers Soil and Plant Analysis Laboratory. Nutrient content will then be compared within and between subsurface gravel wetlands using repeated measures ANOVAs.

Due to construction delays, sampling of vegetation has not yet begun. Construction on the gravel wetlands is scheduled to begin the week of May 19, 2014. I expect to start monitoring plant growth in July with non-destructive sampling (stem counts, measurements of maximum height) taking place monthly from July to November and biomass sampling planned for August and November.

Principal Findings and Significance – N/A project not yet started due to construction delays

Implications of historical and modern land use: urban wetland vegetation as indicators of temporal and spatial environmental heterogeneity and disturbance

Basic Information

Title:	Implications of historical and modern land use: urban wetland vegetation as indicators of temporal and spatial environmental heterogeneity and disturbance
Project Number:	2013NJ342B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-006
Research Category:	Water Quality
Focus Category:	Wetlands, Hydrology, Acid Deposition
Descriptors:	
Principal Investigators:	Laura Shappell, Lena Struwe

Publications

1. Shappell, L. J.* May 20, 2014. Poster: Hope on the Invasion front of Japanese stiltgrass. Joint Aquatic Science Meeting, Portland, OR.
2. Shappell, L. J.* May 14, 2014. Poster: Hope on the Invasion front of Japanese stiltgrass. 99th Annual Conference, New Jersey Water Environment Association. Atlantic City, NJ.
3. Shappell, L. J.; L., Struwe*; J. G., Ehrenfeld. July 2013. Oral Presentation: Japanese Stiltgrass Dominance as a Reflection of Flooding in Headwater Wetlands, in Botanical Society of America, Annual Meeting. New Orleans, LA.

PROJECT SUMMARY

Research Problem

Wetland system structure and function is determined largely by local hydrology and landscape setting. However, land use legacies are pervasive in New Jersey headwater wetlands, whereby altering ecosystem services, such as floodwater storage. Vegetation structure and invasive species dominance is reflective of these modern and historic anthropogenic disturbances. Spatiotemporal models linking species distribution and biophysical features are crucial for understanding the dynamics of ecosystem structure and function. This research builds upon vegetation structure, floristic diversity, and invasive species dominance surveys I have conducted in six urban wetland fragments, located within Middlesex and Union counties. The nonnative invasive, C4, shade-tolerant grass, Japanese stiltgrass (*Microstegium vimineum*) serves as a case study for preliminary analyses. My ongoing research will result in a predictive process model for the complex relationship among hydrology, anthropogenic disturbances, and expressed vegetation community. Additional climate and geophysical landscape data have been incorporated using a geographical information system (GIS). Using Bayesian statistical methods, I will evaluate abiotic traits (e.g., hydrology) and geographic spatial data to examine potential mechanisms behind invasive dominance and floral diversity in urban headwater wetland swamps. Interdisciplinary collaboration for my preliminary dissertation research has highlighted the need for locally dependent wetland flood and invasive species management. *This study will address the need for innovative and holistic management measures for wetland structure and function in an urban watershed.*

Objectives & Research Questions

1) Characterize wetland hydroperiod at sites previously surveyed for vegetation structure.

   What is the nature of the hydrologic conditions (flooding duration, depth, and frequency) within and among my wetland sites?

   How do surrounding land cover and historical modifications, such as ditching, influence urban wetland hydroperiod?

2) Create a predictive process model, incorporating my point-specific field data set with environmental variables that may be influencing ecological processes.

   How does landscape position influence wetland-flooding conditions, and to what extent may position be a predictor for invasive plant species presence?

   Is floristic diversity and species composition reflective of urban wetland hydroperiod?

   To what degree is invasive plant species dominance reflective of historical and modern disturbances in urban wetlands?

Methods

This study is located within the Arthur Kill and Lower Raritan Water Management Areas of central NJ. Six urban headwater wetland fragments within Middlesex and Union counties were selected based on size and dominance of adjacent medium/high density residential land use. Agricultural land use legacies are prominent in nearly all study sites, though much of the area became fallow by the mid-1900s. Dominant plant assemblages within the research sites include deciduous swamps, scrub-shrub, and emergent. Hydroperiods range from saturated to seasonally flooded (Cowardin et al., 1979). Fragment sizes are categorized as large (>125 ha, n=2), medium (<35 ha, n=2), and small (<15 ha, n=2). Sample point placement for the wetland vegetation surveys (2008-2010) were distributed along a 400-m grid (n=35, 707 m^2-sampled plots). Floristic diversity, vegetation structure, and invasive plant species dominance were assessed within each plot. Ecotones water level monitors were deployed within all six wetlands for the 2012 and 2013 season (15 plots).

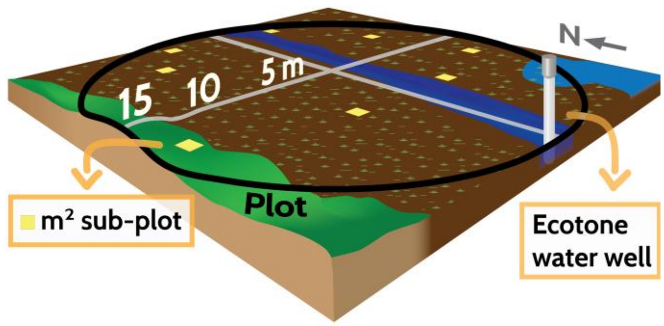


Figure 1: Schematic of vegetation plot and Ecotone data logger placement within study sites. Previous topography surveys were conducted along cardinal transects at 5-m intervals, and groundcover estimates conducted in eight m^2 subplots. NJWRRI-funded follow-up surveys in 2013 of stiltgrass cover and topography followed similar methods.

Data: To build the model I will use my point-referenced, site-level data, including species abundance or presence/absences data, hydrology, and environmental variables. Additional data for each point will account for climate, geophysical landscape, broad hydrologic processes, and LULC (Figure 2). These data will be accessed at the Rutgers University Center for Remote Sensing and Spatial Analysis (CRSSA) using geographical information systems (GIS). Data sources from federal (e.g., USGS, EPA, U.S. Census), NJ state (e.g., NJDEP), and CRSSA (e.g., NJ historical aerials and land classification) will be used to help assess environmental health and historical disturbances.

Models: Hierarchical datasets are more frequently being analyzed within a Bayesian statistical framework because it incorporates prior assumptions (e.g., variance), which enables a better fit for spatially explicit ecological data (Carroll et al., 2010). These methods have been used to analyze and predict invasive species distribution using large spatial data sets such as the Invasive Plant Atlas of New England (Ibáñez et al., 2009). I will use generalized linear models, generalized additive models, and novel Bayesian predictive process models (Latimer et al., 2009). Multivariate and regression analyses will be used to identify key explanatory variables (e.g., hydroperiod, 1930s land use) relative to species distribution for use in

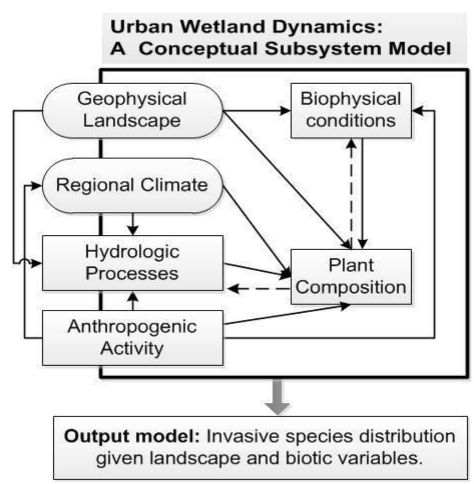
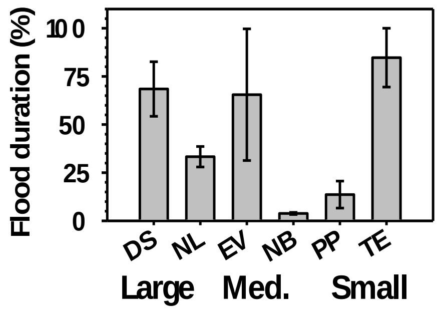


Figure 2: The above conceptual diagram depicts mechanisms that drive my research questions. Rectangles: data types collected for my dissertation.

the models. Spatial autocorrelation and model sensitivity will also be assessed. R statistical software will be used for spatial data analysis (R Core Team, 2012).

Ensemble models will be used for model comparison, and to determine which configuration has the greatest performance. Because models analyze point data differently, the use of ensemble models significantly substantiates the results. The predictive ensemble model will be used to estimate invasive species occurrence within the landscape based on the validated explanatory model. Models produced from this proposal will also examine invasive species distribution and spread relative to site conditions (e.g., hydrology), as proposed in my objectives. Regional-scale presence models and local-scale spatial models are much-needed tools in urbanizing landscapes to minimize cost and effectively implement Best Management Practices.



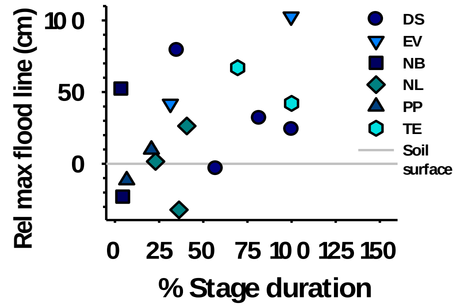


Figure 3: (left) Percent stage duration for Large (DS, NL), Medium (EV, NB), and Small (TE, PP) wetlands. Aboveground flooding varied among, and within size classes (Mean ± SEM). **Figure 4:** (right) mean 2013-2013 flood stage duration and relative plot peak (max) flood depth. Above zero on the y-axis indicates some areas of the 707-m^2 plot were *above* the peak flood line.

Additional statistical analyses: The following methods will be employed to identify variables with the greatest predictive power, in accordance with my stated objectives and research questions. Multiple regression analysis will be used to highlight flooding and landscape properties (e.g., LULC) that are correlated with dependent variables (e.g., species presence). Logistic regression will be employed to test the relationship among independent abiotic variables and expressed biotic variables.

Principle findings and significance

Object 1: Characterize hydrology.

Ecotone water wells recorded data hourly for an average deployment duration of 139 days (SE ± 7.7 days), June-November 2013. Hydrology monitoring equipment deployment was complete for 12/15 wells by mid-June; all equipment was retrieved by mid-November 2012. Three wells were sent for replacement, causing their deployment to be delayed. I am working with the Ecotone well manufacturer to retrieve data from three of this season's wells that are responding to the PDA connection.

Descriptive summaries for each wetland are presented in Table 1; data therein include aboveground flooding duration, frequency, and maximum depth of flooding. Mean percent stage duration varied greatly among wetlands, and within wetland size classes (Figure 3). Summary data of 2012 and 2013 growing seasons are presented in Table 2; combined mean flood stage duration and relative max flood depth are graphed in Figure 3. Maximum flood depth was combined with prior, plot-scale topography measurements to obtain a relative maximum flood depth for a given plot (Rel Max = Flood max – topo range).

Table 1: 2013 Descriptive statistics of Ecotone aboveground water level monitors for each wetland. Flood depth data were calibrated with zero being soil surface. *Monitoring days were excluded from analysis of some wells due to damage or being knocked over. N = number of Ecotone water-wells per wetland.

	N	Days monitored*	Flood: Duration (% days)		Frequency (days)		Max flood depth (cm)	
			Mean ± SE	Min - Max	Mean ± SE	Min - Max	Mean ± SE	Min - Max
Dismal	2[1]	110 – 136	71±65.2	5.63-136	5±3.5	1-8	34±15.6	1.1-71.5
Nom./Lenape	3	157	6±1.6	3.07-7.78	11±1.9	9-15	43±20.4	4.1-72.9
Evergreen	2	110-171	86±83.9	2.22-170	6±4.5	1-10	21±20.6	0.5-41.6
North Bruns.	1[1]	108	1.33		6	6	0.1	0.1
Terrill	2	157	83±74.1	8.82-157	6±5	1-11	61±22.2	38.9-83.2
Polansky	2	110-143	3±1.9	1.3-5.13	9±1	8-10	13±13.1	0.4-26.5

[1] I am troubleshooting data retrieval for two wells from Dismal and one well from North Brunswick, therefore, those data are not included here.

Table 2: Descriptive statistics of Ecotone aboveground water level monitors for each wetland, combined 2012 and 2013 monitoring season averages. Flood depth data were calibrated with zero being soil surface.

	N	Duration (# days)		Relative Dur. (% days)		Max flood depth (cm)		Flood frequency #
		Mean ± SE	Min - Max	Mean ± SE	Min - Max	Mean ± SE	Min - Max	Mean ± SE
Dismal	4	38±31.3	5-132	68±14.2	35.1-100	29±11.4	1.1-48.4	8±2.5
Nom./Lenape	3	5±0.1	4.7-5	33±5.3	23-40.7	24±12.2	2.3-44.5	13±0.6
Evergreen	2	48±45.3	3-93	66±34.2	31.3-99.7	30±2.2	27.6-32	9±4.5
North Bruns.	2	2±0.7	1.8-3.1	4±0.5	3.3-4.4	3.0±2.4	0.5-5.2	16±3.3
Terrill	2	63±49.3	14-113	85±15.3	69.5-100	50±18.8	31.4-69	5±3.8
Polansky	2	4±2.4	1.7-6.4	14±7	6.6-20.6	13±13.1	0.4-26.5	8±2.8

Object 2: Invasive dominance, hydrology, and spatial modeling.

Japanese stiltgrass was the most prevalent invasive species, found at eight of the 15 sample points presented here. Prior to receiving NJWRRI funding I conducted extensive field surveys (84 vegetation plots), and conducted a manipulative mesocosm experiment using stiltgrass as the model species. In the experiment, I manipulated flooding depth or duration (9 treatments, including a control, 7 replicates each). Results from this experiment indicate that as little as four days of aboveground, shallow flooding can inhibit stiltgrass seedling production.

This past growing season I collected updated data on stiltgrass cover (%) within Ecotone monitoring plots (occurred in 8 of 15 plots; see appendix for photos). With these new data, combined with the 2012 relative maximum flood depth, I was able to conclude that stiltgrass distribution is limited to areas above the relative peak flood line (Figure 5). The 2012 flood-monitoring season captured the fall months when stiltgrass sets seed (Sept.-Oct.), and was therefore more representative of stiltgrass cover than the 2013 hydrology dataset.

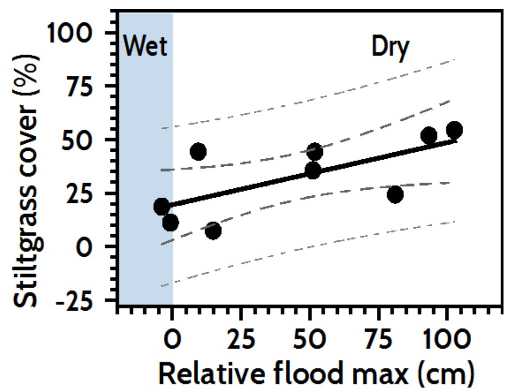


Figure 5: Linear regression analysis of field data indicated stiltgrass cover increased with distance from the relative maximum flood line (Cover = 19.601 + 0.291(Rel max flood); $F_{1,7} = 6.138$, $p = 0.042$, $r^2 = 0.467$).

Incorporating plot topography with flooding data was an important factor because stiltgrass will persist on hummocks that do not experience flooding; this also helps correct for water well placement, which was at the lowest point within each plot. Further analyses will incorporate additional environmental data and the extent to which present and past human modifications such as ditching, or historical land use may influence the modern expressed plant community and local flooding conditions.

Remaining grant funds will be used to process nutrient analyses of soil within the Ecotone monitoring plots, and pay for upcoming conference attendance (see below).

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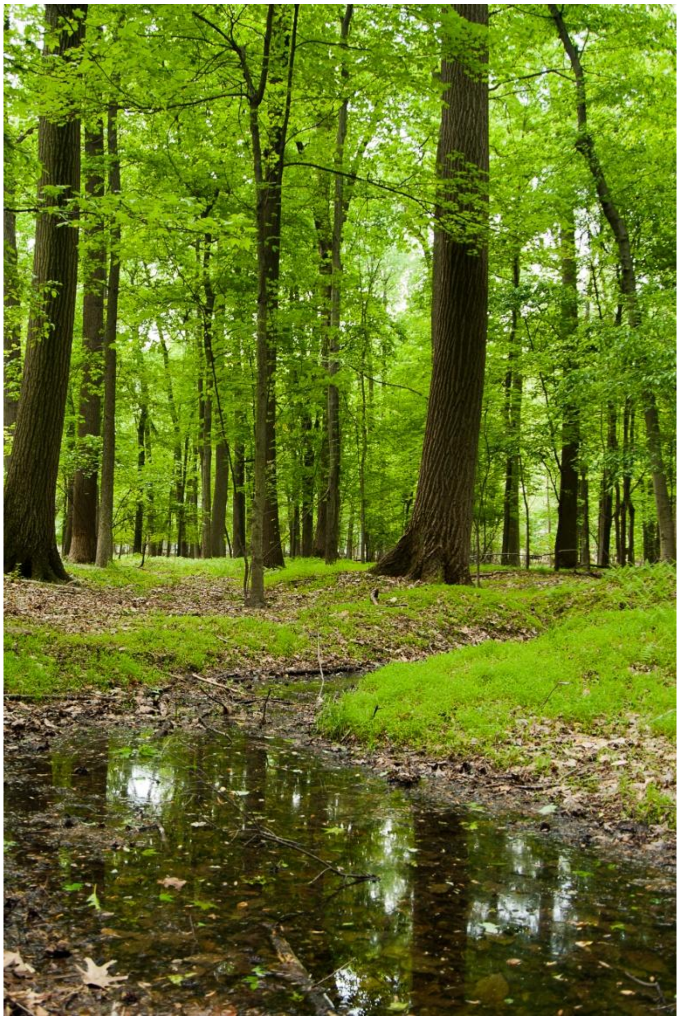
Appendix

Image right: stiltgrass seedlings observed germinating in the early spring, above the ephemeral flood line. This population will not migrate into the flooded area even after drawdown later in the summer.



Below, native cinnamon fern surrounded by a carpet of invasive Japanese stiltgrass in a saturated forested wetland.

Bioaccumulation of mercury in New Jersey aquatic ecosystems

Basic Information

Title:	Bioaccumulation of mercury in New Jersey aquatic ecosystems
Project Number:	2013NJ343B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-010
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, Ecology, Water Quality
Descriptors:	
Principal Investigators:	Natalie Sherwood, Meiyin Wu

Publications

1. Sherwood, Natalie, and Meiyin Wu. April 12, 2014Mercury Contaminant of Snapping Turtles in New Jersey, 8th Annual Student Symposium, Montclair State University, NJ.
2. Sherwood, Natalie, Meiyin Wu and Peddrick Weis. October 16, 2013. Contaminant Transport in Aquatic Food Webs, NJDEP Retreat, Sandystone, NJ.
3. Sherwood, Natalie, and Meiyin Wu. April 4, 2014Mercury Contaminant of Snapping Turtles in New Jersey, Society of Wetland Scientist, State College, PA.

Project Summary:

Mercury is the second contaminant of concern for the Environmental Protection Agency (EPA). Mercury is mainly ingested through the consumption of fish and other aquatic animals. Mercury can possess many serious threats to humans. Humans risk ingesting high levels of mercury trough the consumption of contaminated food, especially seafood. Once ingested, mercury acts as a neurotoxin, first attacking the brain and the nervous system. Ingestion of mercury is most dangerous for pregnant women and young children. Pregnant women are at a significantly higher risk because mercury levels in cord blood are almost twice as much as the mothers (Megler et al. 2007). In adults, mercury consumption can result in neurotoxicity, damaging motor, psychomotor, visual and cognitive functions. Studies have also shown adults to suffer from cardiovascular diseases such as coronary heart disease, ischemic heart (Clarkson, 1992).

A prior study found diamondback terrapins at Cape May had higher mercury concentrations than Meadowland terrapins (Sherwood, et.al, unpublished data). The results suggested that food web dynamics, and mercury contamination levels can vary among different habitat types. Therefore, due to the complexity of aquatic food webs, turtles trophic position, mercury concentrations found in their tissues, and their availability in the market for human consumption, this study will use snapping turtles (*Chelydra serpentina serpentina*) as a representative predator of the aquatic food web. Being at the top of the food chain, snapping turtles bioaccumulate contaminants and are therefore known as good bio indicators for pollutants. Several studies have reported mercury and other contaminants in snapping turtles. Mercury levels in fish and turtles for consumption are regulated by both the US Food and Drug's Action Limits (USFDA) and the Environmental Protection Agency (EPA). The US EPA mercury threshold for recreationally harvested food is 0.3ppm.

The common snapping turtle is one of the largest freshwater turtles in the US, its long-lived (up to 50 years) and reaches sexual maturity late in life (Congdon et al., 1994; Golet and Haines, 2000). The snapping turtle and diamondback terrapins have a unique ability to adapt to humans and the changing environment, since they have been observed in polluted and urban waters. Snapping turtles are also important scavengers and predators, consuming rotting meat and variety of fish and plants. Turtle food items to be caught and collected for mercury testing are fish (carp, shiners, sunfish, catfish), frogs (spadefoot toad, true toad, cricket frog, tree frogs, chorus frog), salamanders (brook salamanders, red salamanders), small turtles (mud turtles, musk turtles, painted turtles, cooters, sliders), algae (waterweeds, pond weed, knotweed, water lily, duckweed, cattail).

In New Jersey the turtle harvest is under the jurisdiction of the Department of Fisheries. The state currently allows both recreational and commercial harvesting for snapping turtles and recreational harvesting for diamondback terrapins. In recent years the demand for turtles has increased and also has the demand for commercial harvesting permits for snapping turtles. Due to the increasing demand of turtle meat it is important to understand the food webs bioaccumulation and magnification factors.

We suggest studying mercury concentration in aquatic food chain to better understand contaminant transfer from one trophic level to the next. We will be collaborating with the New Jersey Department of Fisheries and New Jersey's Endangered and Nongame Species Program. This study will be important in advancing the knowledge and understanding of the bioaccumulation and biomagnification effects of mercury contamination in the aquatic food web.

Methodology

Hoop traps and minnow traps will be placed at study sites, traps will be surveyed every day. Turtles found in traps will be measured, weighed, and sexed. Tissue and blood samples will be collected. A 0.25g tissue sample will be collected from various body parts. For turtles samples will be collected from tail, shell and blood will also be collected. Blood samples will be collected using a 16gauge needle. Tail muscles samples will be collected by first anesthetizing the area and using a scalpel and curved scissors to extract the sample. Vet bond will be applied to the incision and animals will be held for approximately 15min for observation. A scalpel will also be used to scrape a thin keratin layer off the carapace. When possible we will avoid sacrificing any animal instead we will collect toe and tail clips to be tested for mercury concentrations. Frogs and salamanders will be collected opportunistically by hand. We suggest taking toe and tail clipping for frogs and salamanders sample collection. Vet bond will be applied to the incision areas. Fish will be measured and taken back to the lab where they will be filet. Algae and other plant materials will be collected at each site. All samples collected will be placed in zip lock bags and kept in ice until arrival at Montclair University where they will be processed. NJDEP scientific collection permits have been granted to collect animals. Additionally, animal care and collection protocols have been reviewed and approved by the Montclair State University's Institutional Animal Care and Use Committee.

Samples will be weighed and placed into clean test tubes and covered with parafilm. The samples will be transported in ice to a laboratory located at the University of Medicine and Dentistry of New Jersey to be analyzed for mercury concentrations using a cold vapor atomic absorption spectrophotometer in a MAS-50D mercury analyzer (Bacharach, Inc.).

Principal Findings and Significance:

This study is still in progress. Twenty-nine snapping turtles were caught at the School of Conservation. Nine snapping turtles were collected from Liberty State Park. Four snapping turtles were collected from the Kearny Marsh. Due to the high incidents of stolen traps at the last site we will no longer be trapping but will rather focus on road mortality. Overall, 78 turtle samples were collected and analyzed. Seven road casualties were also collected from the Kearny Marsh area. Data is presented in Table 1. The results demonstrated 55% of snapping turtles caught at Liberty State Park had detectable mercury levels in their blood, 30% at the School of Conservation, and 25% at the Kearny Marsh. All blood samples were below the EPA threshold limit for mercury of 1ppm. 96% of all carapace samples collected at the School of Conservation were above the EPA threshold. All carapace samples collected from turtles from Liberty State Park and 75% of the samples collected at the Kearny Marsh were above the EPA threshold. Muscle samples with mercury concentrations above the detection limit were found at the School of Conservation and Liberty State Park. The mercury sample collected at Liberty State Park was found to be above the EPAs threshold with a concentration of 0.724 ppm. Samples for primary producers (PP), primary consumers (PC), and secondary consumers (SC) are yet to be analyzed.

Table 1. Snapping turtle measurements and mercury data.

	Hg Blood			
Site	**N**	**Mean**	**Max**	**Min**
Lake Wapalanne	10	0.071	0.243	0.013
Liberty State Park	5	0.051	0.069	0.03
Kearny Marsh	2	0.021	0.042	<0.0049

	Hg Carapace			
Site	**N**	**Mean**	**Max**	**Min**
Lake Wapalanne	27	0.659	1.278	0.176
Liberty State Park	5	0.056	0.268	<0.0049
Kearny Marsh	3	0.440	0.591	0.359

	Hg Muscle			
Site	**N**	**Mean**	**Max**	**Min**
Lake Wapalanne	4	0.061	0.242	<0.0049

Liberty State Park	1	0.724	0.724	-----
Kearny Marsh	0	------	-----	-----

Dehalogenation of halogenated aromatic compounds by indigenous microorganisms in sediments of the Hackensack River, New Jersey

Basic Information

Title:	Dehalogenation of halogenated aromatic compounds by indigenous microorganisms in sediments of the Hackensack River, New Jersey
Project Number:	2013NJ344B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-006
Research Category:	Water Quality
Focus Category:	Sediments, Toxic Substances, Water Quality
Descriptors:	
Principal Investigators:	Seo Yean Sohn, Max M Haggblom

Publication

1. Seo Yean Sohn and Max Haggblom, 2013, Dehalogenation of halogenated aromatic compounds by indigenous microorganisms in sediments of the Hackensack River, New Jersey, Gordon Research Conferences: Applied & Environmental Microbiology, 07/07/2013 - 07/12/2013, Mount Holyoke College in South Hadley MA United States

(4) Project Summary

Problem and Research Objectives

The Hackensack River is approximately 45 miles long flowing from southeastern New York into Newark Bay, NJ. Once it had supplied clean water to residents. However, after constructing the Oradell reservoir, the water quality of Hackensack River became worse. Furthermore, the lower part of the Hackensack River, the Hackensack Meadowlands was a hotspot of garbage dumping by factories and municipalities. As a result, the river is contaminated by pollutants such as PCBs and polychlorinated dibenzo-*p*-dioxins. PCBs and dioxins are well-known examples of organohalides, which are of concern because of their persistence in environment. Recently, organobromides have become of concern with the extensive use of brominated flame retardants (BFRs). In river environments, these chemicals accumulate in sediments due to their low solubility in water and sorption onto particulate material. However, the compounds can dissolve in lipid freely, thus they can be bioaccumulated and biomagnified in the food chain. As a result, fish living in Hackensack River are contaminated by organohalides and for public health reasons it is prohibited by the state to eat the fish caught from the river. The water quality of the river can influence the diversity of the birds as well because they ingest the contaminated fish. Even though the Clean Water Act has contributed to improving water quality of the Hackensack River, sediments can be a reservoir of contaminants. Therefore, the water quality of river has to be controlled and improved.

A microbial approach to remediate river environments can be a better alternative than traditional dredging and treatment techniques. First of all, dredging can be harmful to environmental remediation. By stirring the bottom of the river, settled pollutants can be distributed and mixed with cleaner portions of the river. The second fact to support microbial remediation technique is low oxygen level of the Hackensack River. There is a trend that as numbers of halogens decrease, the toxicity of the compounds decreases. Less halogenated aromatic compounds can also be a target to aerobic bacteria which degrade the compounds completely by breaking aromatic ring. It has been demonstrated that microbial reductive dehalogenation is effective in dehalogenating organohalide pollutants. In the case of reductive dehalogenation, a low oxygen level can be a good condition, which can promote the activity of dehalogenating bacteria.

The objective of this study is to understand the dynamics of dehalogenating bacteria in the river sediment. Hexachlorobenzene (HCB), hexabromobenzene (HBB), and pentachloroaniline (PCA) are selected as model compounds to induce dehalogenating bacteria.

Methodology

The Hackensack River sediments were collected from five different locations (H1 to H5; the uppermost to the lowest reaches of the river) to set up microcosms. Three halogenated compounds, HCB, HBB, and PCA, were added as a model compound to understand the activity of dehalogenating bacteria. Treatments were triplicated. Unamended controls and killed controls were also prepared. Culture preparation was performed in an anaerobic chamber. Samples were collected every 2 weeks to monitor for dehalogenating activity. Extracts were analyzed by gas chromatography with a mass selective detector.

PCR-DGGE was done with DNA extracted from cultures of H1 and H5. Nested PCR was performed to amplify specific region of 16S rRNA gene of *Chloroflexi*. PCR products were run on DGGE (density gradient gel electrophoresis). Prominent bands from the gel were excised. They will be sequenced to see what organisms are involved in dehalogenation at each location.

Carbon isotope fractionation experiments are performed to distinguish whether decrease of contaminants is caused by abiotic factors or microbial remediation. Microorganisms prefer to break weaker bonds to gain energy. Since lighter atom makes a bond weaker, microorganisms will use ^{12}C at first and it makes ^{13}C accumulated. Cultures were prepared for carbon isotope fractionation experiments. Four chlorobenzenes and two bromobenzenes were selected for substrates based on the result of intermediates of HCB dehalogenation. They were hexachlorobenzene, pentachlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,5-tetrabromobenzene and 1,3,5-tribromobenzene. Two cultures were sacrificed for extraction at each time point. Isotope fractionation experiment was done at UFZ, Leipzig-Halle.

Principal Findings and Significance

Microcosms set up with the Hackensack River sediment were capable of dechlorinating HCB and PCA. HCB was dechlorinated to diCB via 1,3,5-triCB. There was a delay of dehalogenation from the culture contained the sediment from H5.

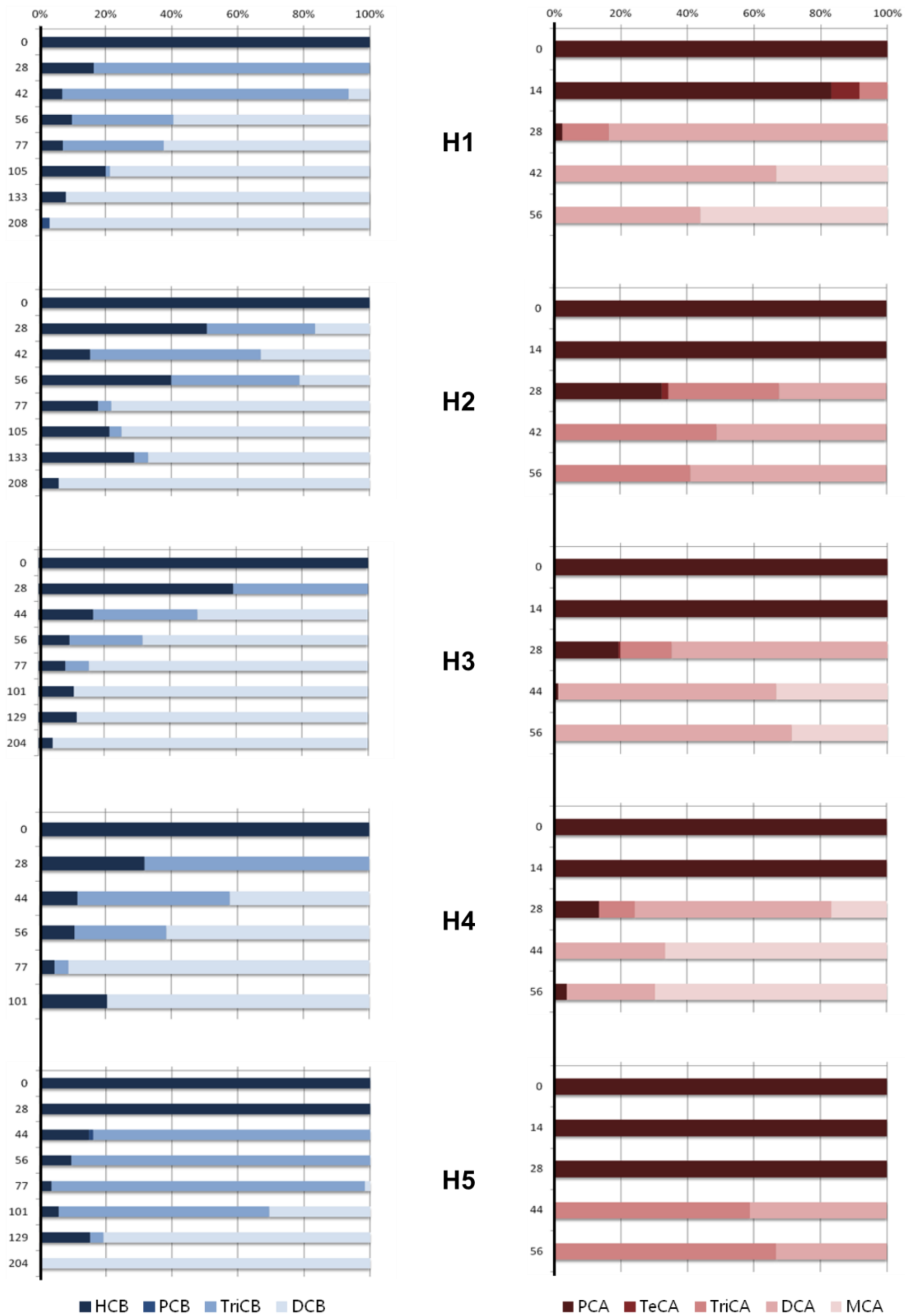


Fig 1. Dehalogenation of HCB and PCA.

X axis represents mol percentage and Y axis represents days.

DGGE showed different results between two sampling locations, H1 and H5. There was an induction of *Chloroflexi* from HCB and PCA treated microcosms from H1. However, no induction of *Chloroflexi* was observed in microcosms from H5. *Dehalococcoides* spp. are known for its capability of dehalogenation and they are under the *Chloroflexi* phylum. A unique characteristic *Dehalococcoides* has is that they have few tenths of various reductive dehalogenase (*rdh*) genes on their genome. Therefore, it is possible that *Dehalococcoides* dehalogenates a variety of halogenated compounds. Since the Hackensack River is known to be polluted by PCBs and dioxins, its sediment can be a habitat of *Dehalococcoides* species. Thus it is possible that these *Dehalococcoides* species dechlorinating PCBs or dioxins also dehalogenate a variety of halogenated compounds. Furthermore, based on the DGGE result, we can expect that there are bacteria other than *Dehalococcoides* involved in dehalogenation of HCB and PCA at the lower reaches. It needs to be determined which bacteria are responsible for dehalogenation at the site.

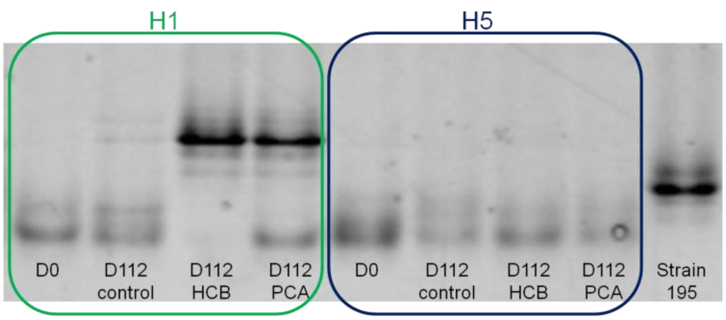


Fig 2. *Chloroflexi* community analysis with Nested PCR and DGGE.

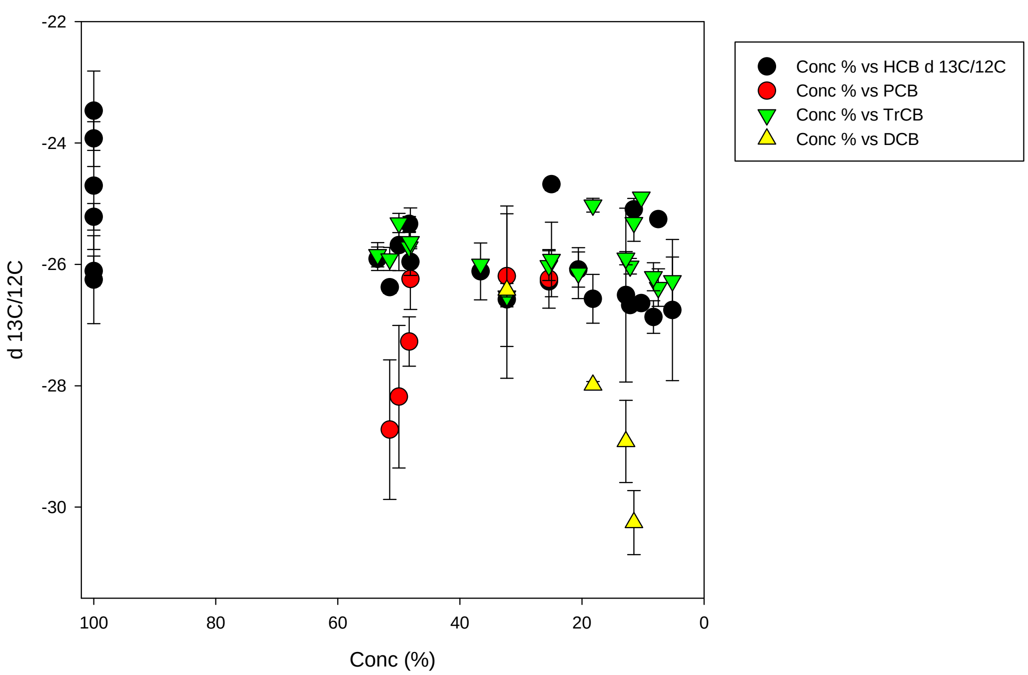


Fig 3. Result of isotope analysis. The data need to be analyzed.

Biodegradation of polycyclic aromatic hydrocarbons in the Barnegat Bay-Little Egg Harbor estuary

Basic Information

Title:	Biodegradation of polycyclic aromatic hydrocarbons in the Barnegat Bay-Little Egg Harbor estuary
Project Number:	2013NJ345B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-006
Research Category:	Water Quality
Focus Category:	Treatment, Toxic Substances, Non Point Pollution
Descriptors:	
Principal Investigators:	Sarah J Wolfson, Lily Young

Publication

1. Wolfson, Sarah; Young, L.Y. 2014. 2014. Anaerobic degradation of naphthalene by a sulfate-reducing marine community. American Society for Microbiology General Meeting 2014, Boston, Massachusetts. Poster Presentation.

(3) **Project Summary**:

Anaerobic degradation of naphthalene by a sulfate-reducing marine community
The widespread use of petroleum for fuel, pesticides, and numerous other applications has caused ubiquitous contamination of polycyclic aromatic hydrocarbons (PAHs) in the environment. PAH deposition has been demonstrated in NJ and along the Mid-Atlantic coast, including Barnegat Bay and Little Egg Harbor (1).

This project investigates microbial communities in the BB-LEH estuary responsible for the biodegradation of PAHs. The introduction of PAHs to the estuarine ecosystem occurs through a variety of sources, including atmospheric deposition, leachate from creosote treated marine lumber, and powerboat emissions (1, 2). PAHs have mutagenic and carcinogenic properties, and are capable of biomagnification up the food chain (3). Microbes are the only organisms able to utilize hazardous chemicals such as PAHs for food and degrade the contaminants to innocuous products such as cells, CO_2 and H_2O (5). Their potential ability to naturally remediate PAHs and other pollutants may maintain the integrity of the ecosystem. This study will determine whether microbes capable of PAH degradation are present in the BB-LEH estuary, identify potentially novel bacteria responsible for this metabolic activity, and isolate both intermediate metabolites and molecular biomarkers specific to PAH biodegradation. The isolation of signature biomarkers would provide tools to monitor *in situ* PAH bioremediation.

Because the BB-LEH estuary is a shallow, poorly flushed system, it is vulnerable to contaminant accumulation. The following objectives were investigated: (1) Determine whether microbes indigenous to an estuary receiving continual, nonpoint PAH contamination are capable of consuming naphthalene as a carbon source under sulfate reducing conditions. (2) Analyze naphthalene degrading microbial community structure and function

Methods

Sediment Free Transfer Enrichment Cultures
Primary enrichment cultures growing on naphthalene under sulfate reducing conditions were transferred and refed 500uM naphthalene. Naphthalene concentration was measured using GC/FID. Sulfate was measured using IC.

Molybdate Amended Cultures
To determine coupling of naphthalene loss to sulfate reduction, the sulfate reduction inhibitor molybdate was added at equal concentrations to sulfate (28mM) in defined media. 250uM naphthalene was provided as the sole carbon source. Duplicate active and uninoculated sterile control cultures were established.

Molecular Analysis
DNA was extracted from enrichment cultures using MoBio DNA PowerSoil (Carlsbad, CA). NaphS2 phylotype16S primers (NaphF, 907R) were used to probe for the naphthalene degrading isolate NaphS2.

Results

Complete naphthalene loss was seen after 139 days in primary enrichment cultures. Primary transfer cultures degraded naphthalene within 48 days (Figure 1). Naphthalene was fully degraded by subsequent enrichment cultures after 20 days, and stoichiometric sulfate loss to complete naphthalene degradation was observed in enrichment cultures (Table 1).

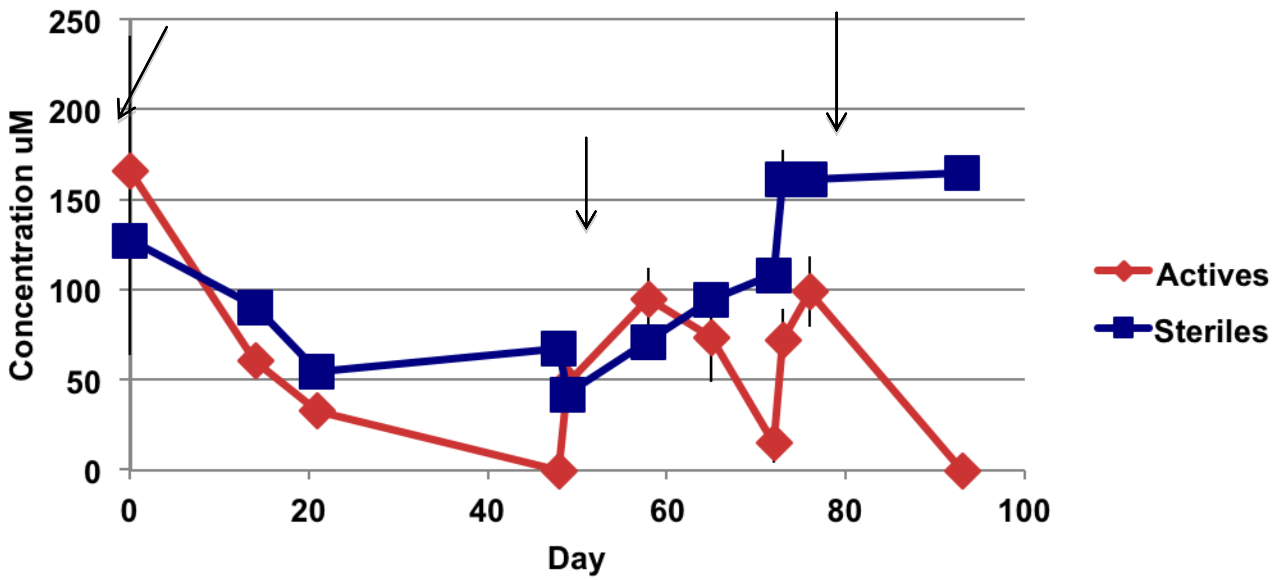


Figure 1. Naphthalene degradation in transfer cultures. Arrows indicate refeeding. Cultures were transferred on day 0 and day 72.

	Predicted SO_4^{2-} Loss (mM)	Observed SO_4^{2-} Loss (mM)
Active Cultures	3	3 (±1.2)
Uninoculated Controls	0	0 (±0)

$$C_{10}H_8 + 6SO_4^{2-} \rightarrow 10CO_2 + 6H_2S + 4H_2O$$

Table 1. Predicted and observed sulfate concentrations in active and uninoculated control transfer cultures.

Molybdate Amended Cultures

Complete naphthalene loss was seen in subcultures unamended with molybdate in 6-13 days. No decrease in naphthalene degradation occurred in cultures amended with 28mM molybdate (Figure 2).

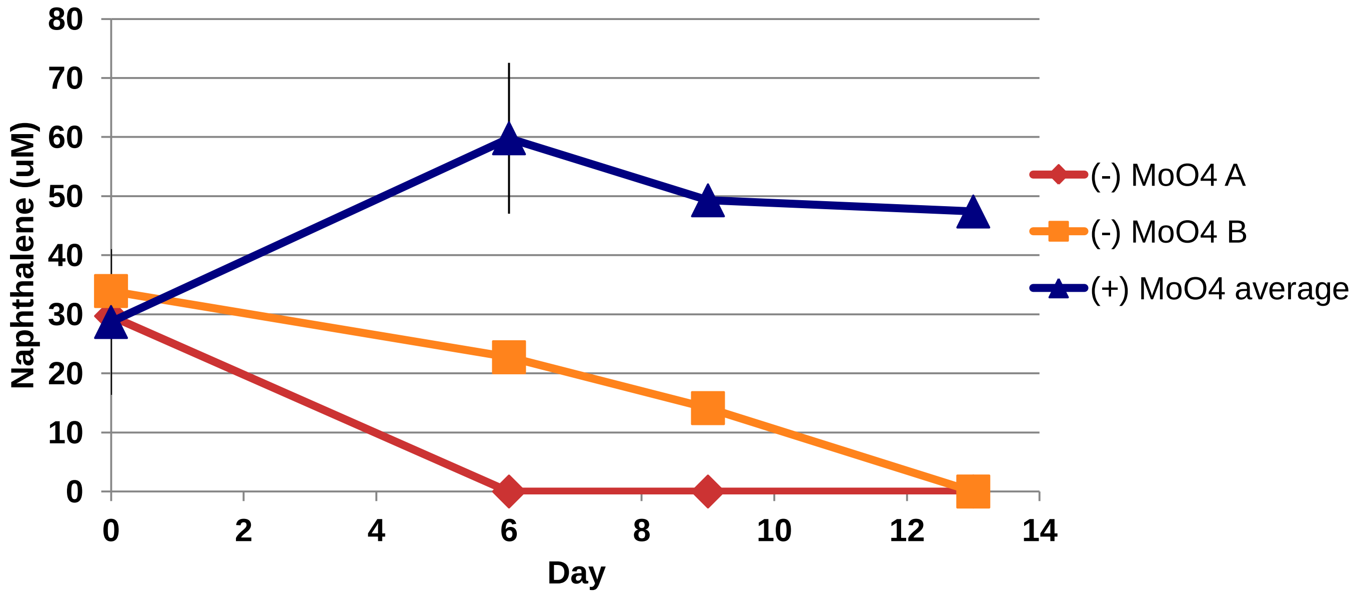


Figure 2. Naphthalene degradation with and without molybdate. (+)MoO_4 subcultures received 28mM molybdate, equivalent to the sulfate concentration in culture.

NaphS2 Phylotype Molecular Analysis

No amplification of NaphS2 phylotype 16S rDNA was seen in enrichment cultures capable of naphthalene degradation (Table 2). 16S rDNA from the NaphS2 phylotype was amplified from a boat basin and locally contaminated sediment within JCNERR. No amplification was seen in *Spartina* marsh sediment.

	Enrichments	Boat Basin	Contaminated sediment	Marsh sediment
NaphS2 Phylotype	-	+	+	-

Table 2. Presence of NaphS2 phylotype in enrichment cultures and microenvironments within JCNERR. Environmental samples include the Rutgers University Marine Field Station Boat Basin, which houses 9-13 marine vessels; Contaminated Sediment from a pocket of creosote within the boat basin; Marsh Sediment collected from a *Spartina* tidal marsh.

Conclusions

Naphthalene degradation is coupled to sulfate reduction. Sediment free enrichment cultures, provided with naphthalene as the sole carbon source, degraded naphthalene in 20 days. Stoichiometric loss of the electron acceptor sulfate was observed. The coupling of naphthalene degradation to sulfate reduction was demonstrated in the presence of molybdate, a sulfate reduction inhibitor, as naphthalene degradation did not occur in cultures amended with molybdate. The presence of NaphS2 phylotype 16S rDNA in contaminated marine sediment is consistent with previous studies (4). The absence of this described phylotype of naphthalene degrading isolates in the enrichment cultures suggests undescribed bacteria are responsible for naphthalene degradation.

Naphthalene degrading cultures were enriched from the Jacques Cousteau National Estuarine Research Reserve, a relatively pristine habitat. JCNERR has not been impacted by large scale point hydrocarbon pollution; instead, hydrocarbon contamination is introduced from boat activity, creosote infrastructure leachate, and atmospheric deposition. The presence of naphthalene degrading microbes in historically uncontaminated areas suggests that the indigenous microbial community has selected for microbes capable of PAH degradation.

References

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2. Costa, H. J., and Wade, M. J. Fate and Effects of PAH Leaching from Creosote-Treated Marine Pilings. ASCE *Coastal Zone '89* 1989, 3875-3888.

3. Kanaly R. and Harayama S. Biodegradation of High-Molecular-Weight Polycyclic Aromatic Hydrocarbons by Bacteria. *Journal of Bacteriology* 2000, 182(8): 2059-2067.

4. Hayes, L. A. and Lovely, E. D. R. Specific 16S rDNA sequences associated with naphthalene degradation under sulfate reducing conditions in harbor sediments. *Microbial Ecology* 2002, 43:134-145.

5. Zhang, X and Young, L. Y. Carboxylation as an initial reaction in the anaerobic metabolism of naphthalene and phenanthrene by sulfidogenic consortia. *Applied and Environmental Microbiology* 1997, 63(12):4759-4764.

Information Transfer Program Introduction

The information transfer program serves an important purpose to the state's water resource community. The goal is to bring timely information about critical issues in water resource sciences to the public and to promote the importance of research in solving water resource problems.

Information Transfer Program

Basic Information

Title:	Information Transfer Program
Project Number:	2013NJ346B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	NJ-006
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Christopher Obropta, Lisa Galloway Evrard

Publications

There are no publications.

Information Transfer Program

For FY2013, the information transfer program has emphasized the development of the website and e-based communications with stakeholder groups.

Our website (www.njwrri.rutgers.edu/) has been continually updated with information on water resource events and information in New Jersey, the U.S. and around the world. The home page and 'events' pages are regularly updated to highlight upcoming events, publications and other water–related news. The website is our primary means of information transfer to the water community and the public, and we will continue to update and improve its functionality.

We continue to expand and use targeted, group-specific e-mail lists to bring relevant information to specific audiences. Targeted lists include a list of scientists/principal investigators, water resource managers, non-governmental organizations and people affiliated with NGOs, and policy-makers. The lists are continuously updated and expanded, and are used to keep these groups informed of events, conferences, publications, and funding opportunities. These lists enable us to initiate and maintain frequent contact with stakeholder groups. We believe these lists are an excellent method of keeping the water-related public aware of NJWRRI, as well as informed about water-related news and information.

We also continue to participate in the New Jersey Water Monitoring Council, a statewide body representing both governmental and non-governmental organizations involved in water quality monitoring.

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	0	2
Masters	4	0	0	0	4
Ph.D.	9	0	0	0	9
Post-Doc.	3	0	0	0	3
Total	18	0	0	0	18

Notable Awards and Achievements

For 2013NJ339B: NJWEA Kenneth S. Stoller Award 2014

For 2013NJ342B: First place poster competition winner ($ TBA). May 2014. 99th Annual New Jersey Water Environment Association Conference. Atlantic City, NJ.

For 2013NJ342B: John J. LaGrosa Scholarship Award ($2,500). April 2014. New Jersey Water Environment Association.

For 2011NJ292G: First Place Student Poster Presentation Award, 27th Conference on Hydrology at AMS Annual Meeting, 2013 for: Kam, J., J. Sheffield, E.F. Wood, 2013, An integrative analysis of drought in the southeastern United States, 93rd AMS Annual Meeting, Abstract #221097, January 6-11th, Austin, TX

Publications from Prior Years

1. 2011NJ278B ("Advancing the characterization of sandstone and fractured limestone aquifers using surface electrical geophysical methods: application to water resources evaluation at two sites in New Jersey") - Articles in Refereed Scientific Journals - Elwaseif, M., Khalil, A.M., Hafez, A.M., Advancing the Characterization of Sandstone Aquifers Using Time - Frequency Analysis of GPR Datasets. Submitted to Geophysics 2013 and under revision (GEO-2011-0423).